

Additive controlled crystallization of barium titanate powders and their application for thin-film ceramic production:

Part II. From nano-sized powders to ceramic thin films

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Nano-sized barium titanate (BaTiO_3) particles prepared by the sol-to-precipitate method in aqueous/organic medium served to obtain thin-layer ceramic films of the tetragonal electroactive phase. Poly(methacrylic acid) works efficiently to process the suspensions and to obtain green films. Sintering the green films under O_2 -Ar atmosphere gave thin-layered ceramics of a thickness of 0.5–1.0 mm with a dielectric constant of 3750 at 20 °C (1 kHz).

I. INTRODUCTION

In our previous publication,¹ we have described how nano-sized barium titanate (BaTiO_3) particles are obtained by the sol-to-precipitate method starting from barium hydroxide and tetramethylammonium hydroxide in a medium consisting of carbon dioxide free water and acetone or methanol or a mixture of both. Titanium(IV) triethanol amino isopropoxide was employed as the source of titanium. Typically, narrow size distributions of BaTiO_3 particles with average diameters between 60 to 90 nm were reproducibly obtained. Such nano-sized powders are desirable to fabricate thin-layer electroactive ceramics to be used in miniaturized electronic devices. However, nano-sized powders tend to aggregate in the slurries to form layer-sized objects which in turn lead to inhomogeneous material in the sintering process. Thus, it is important to find conditions under which aggregation is either prevented or minimized by suitable additives. Polymers have been shown to be such additives.^{2–7}

In this work, we demonstrate under what conditions the nano-sized BaTiO_3 particles can be processed to obtain electroactive BaTiO_3 in form of thin films exhibiting optimal dielectric behavior.

II. EXPERIMENTAL

A. Stabilization of powder suspensions

X-ray diffraction (XRD) patterns of synthesized BaTiO_3 powders indicated that BaCO_3 was not formed by adding acetone or methanol concentrations up to 2.8 or 6 mol/l, respectively. Also methanol/acetone mixtures at volume ratios of 1:1, 2:1, and 3:1 and overall concentrations of 2.65, 4.07, and 5.32 mol/l of organic solvent gave precipitates of pure BaTiO_3 .¹ The XRD pattern of a BaTiO_3 powder synthesized by addition of 5.32 mol/l methanol/acetone (volume ratio: 3:1) is shown in Fig. 1(a) and demonstrates the good crystallinity of barium titanate and the absence of BaCO_3 . For the fabrication of powder suspensions barium titanate powders synthesized by adding a methanol/acetone mixture of 2.65 mol/l (volume ratio: 1:1) were used. In the following these powders are termed as BTM.

Aggregate size distributions were determined by adding 100 mg of barium titanate powder BTM to 10 ml of a 0.5 mg/l aqueous polymer solution while the pH was kept constant. Analytical grade HCl and KOH solutions (0.1 mol/l) were used to adjust the pH at 10. After the samples were ultrasonicated for 15 min (25-W system), the pH was measured and adjusted again, if necessary. The samples were put into a mechanical shaker for 24 h to allow for equilibration. After that time the suspensions were diluted with deionized water to 1/10 strength and the aggregate size distribution of barium titanate particles was determined by a disk centrifuge.⁸ The stabilizers were diblock copolymers (DBCP's) consisting of

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hydrophilic poly(methacrylic acid) (PMAA) blocks and poly(ethylene oxide) (PEO) blocks [P(MAA-*b*-EO); GEA18 and EA14], a homopolymer [poly(methacrylic acid), PMAA], and a statistical copolymer [P(SSA-MA)], which is composed of poly(styrenesulfonic acid) and poly(maleic acid) (Table I).

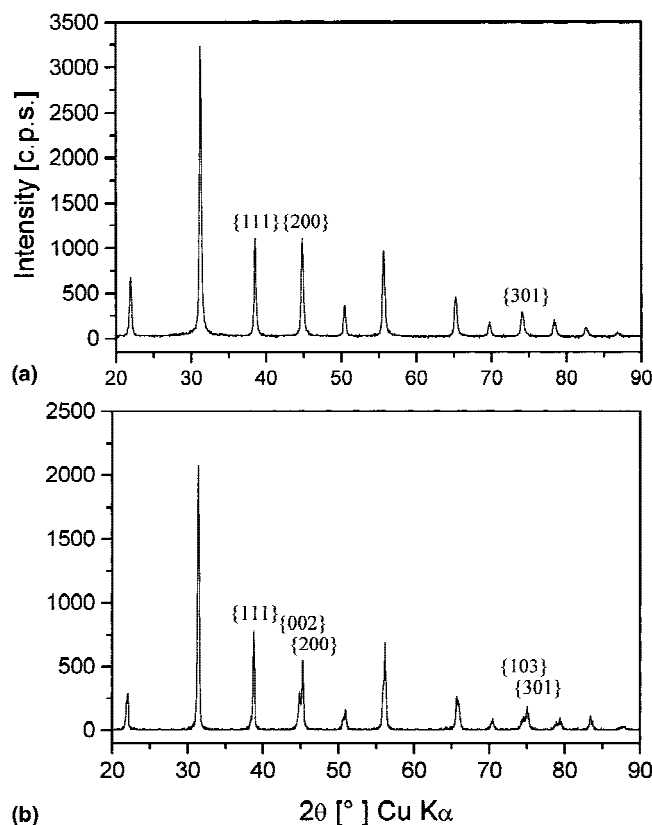


FIG. 1. (a) XRD pattern of a powder synthesized by addition of 5.32 mol/l methanol/acetone (volume ratio: 3:1) and (b) XRD of a sintered green film BTM34min (temperature program: see text; O_2 -Ar atmosphere) prepared by dispersing the powder sample BTM (see text) with an aqueous PMAA solution.

TABLE I. Characteristics of the polymers used as dispersants in powder suspensions.

Polymer ^a	BLR ^b	Molecular weight M_N (g/mol)
PMAA	Homopolymer	2600
P(MAA- <i>b</i> -EO) GEA18	26/270	14100
P(MAA- <i>b</i> -EO) EA14	34/38	4600
P(SSA-MA)	Statistical copolymer	20000

^aPMAA: poly(methacrylic acid). P(MAA-*b*-EO): poly(methacrylic acid-*b*-ethylene oxide); diblock copolymer. P(SSA-MA): poly(styrenesulfonic acid-maleic acid); statistical copolymer.

^bBLR (block length ratio) of the number of monomer units in the hydrophilic (PMAA) and the stabilizing (PEO) blocks.

B. Sintering

Poly(vinyl alcohol) (PVA; M_N 15000, Fluka Chemika) and glycerol (87 wt% in aqueous solution, Merck) were used in the preparation of green films as binder and plasticizer, respectively. In one experiment PMAA was added as dispersant.

The slurry for green films was prepared by adding 500 mg of barium titanate powder BTM to 1 ml of a (1) 130 mg/l or a (2) 5 mg/l aqueous polymer solution, containing (1) 10 mg of PVA and 120 mg of glycerol and (2) 5 mg of PMAA at pH = 10, respectively. After ultrasonication for 10 min (25-W system), the samples were mechanically shaken for 24 h to allow equilibration. In the case of slurry (2) 20 mg of PVA and 140 mg of glycerol were added to the suspensions, ultrasonicated for 10 min, and shaken for 24 h again. Table II summarizes the conditions for preparing green films.

To form green films, the slurries were poured into Teflon moulds and carefully degassed in a desiccator to prevent an increase of defect density of the ceramics by gas bubbles. After being dried in air for 3 days the green films were subsequently heated in a high-temperature furnace under ambient atmosphere using a heating rate of $3\text{ }^\circ\text{C min}^{-1}$ from $25\text{ }^\circ\text{C}$ to the densification temperature of $1250\text{ }^\circ\text{C}$. After 120 min a cooling rate of $5\text{ }^\circ\text{C min}^{-1}$ was applied to bring the samples (BTM34, -36, -37, -38, -39, and -40) back to room temperature. Further samples (for example BTM34min) of the same green films were sintered in a thermoanalytical apparatus (Setaram TG-DTA 92-16) under O_2 -Ar atmosphere at the following conditions: from 20 to $80\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$; from 80 to $120\text{ }^\circ\text{C}$ at $1\text{ }^\circ\text{C min}^{-1}$; from 120 to $550\text{ }^\circ\text{C}$ at $5\text{ }^\circ\text{C min}^{-1}$; from 550 to $950\text{ }^\circ\text{C}$ at $3\text{ }^\circ\text{C min}^{-1}$; from 950 to $1250\text{ }^\circ\text{C}$ at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$. The samples were kept at $1250\text{ }^\circ\text{C}$ for 120 min and were then quenched to room temperature at a cooling rate of $5\text{ }^\circ\text{C min}^{-1}$.

The microstructure of sample surfaces and the phases formed were examined by scanning electron microscopy (SEM; LEO Gemini 1530) and x-ray diffraction (XRD; Philips PW 1820) (Philips Deutschland GmbH, Kassel).

The sintered films were coated with gold on both sides and evaluated by impedance spectroscopy [IS; Solartron SI1260 (Novocontrol GmbH, Hundshagen, Germany), with a broad-band dielectric converter] to determine the dielectric constants (ϵ') at a frequency of 1 kHz at temperatures from 20 to $250\text{ }^\circ\text{C}$.

III. RESULTS AND DISCUSSION

A. Stabilizing aqueous $BaTiO_3$ suspensions

Information on the stability of aqueous $BaTiO_3$ suspensions is very important to the fabrication of green films and the sintering process.⁹ The release of Ba^{2+} ions

from particle surfaces at low pH was described by many researchers, and changes in surface composition were identified as very crucial for sintering properties.^{10,11} However, at $\text{pH} \geq 10$ the stability is sufficient, and only small concentrations of Ba^{2+} could be measured.¹² Zeta potential determinations in the presence and absence of polymers as a function of pH gave the result that a $\text{pH} \geq 10$ is best for the stabilization of BaTiO_3 suspensions.^{12,13}

Aggregate size distributions were determined using the pure BaTiO_3 powder BTM which consists largely of individual spherical particles with a mean particle size of 70.2 nm in diameter (standard deviation: 17.6 nm) and a specific surface area of $15.8 \pm 0.4 \text{ m}^2/\text{g}$.¹ The suspensions were prepared as described in Sec. II.A and the aggregate size distributions determined by a disk centrifuge. The polymers used as dispersants are described in Table I.

The results of the experiments are depicted in Fig. 2. Using the polymers GEA18 and EA14, the size distributions of aggregates become narrower with decreasing length of the stabilizer block PEO. The relatively high molecular weight statistical copolymer P(SSA-MA) and the short homopolymer PMAA gave further reduction of aggregate size distributions. Suspensions prepared with PMAA only showed the narrowest distribution, with a mean aggregate size of approximately 86 nm in diameter, only slightly larger than the mean particle size of BTM powders,¹ giving evidence for dispersed individual particles in the suspensions. As a consequence, BTM powders are only suitable for preparation of slurries and green films of high green densities if PMAA is used as dispersant in small amounts.

At the same weight fraction, the polymer EA14 produces a narrower aggregate size distribution similar to the case for GEA18. The narrowest size distribution is obtained when PMAA is employed. This suggests that polymers of lower molecular weight are more effective than those of high molecular weight. However, the observation that polyacids work as dispersants at all, under the given conditions of $\text{pH} \geq 10$, is somewhat surprising. Naively one would expect repulsive interactions to prevail between the polyanions and the negatively charged particle surface. But, if one takes into account that a very high Ba^{2+} concentration exists near and at the particle

surface, a partial or complete precipitation of the polymer may take place that in turn stabilizes the particles against agglomeration, provided flocculation by bridging effects can be prevented. The latter becomes more and more improbable as the chain length, that is, the molar mass of the dispersants, becomes small.

B. Green film sintering and characterization of the ceramic thin films

BaTiO_3 green films, produced by various formulations as outlined in Table II, were sintered under conditions described in Sec. II.B. The sintered samples were investigated by SEM. Fairly uniform and small grain sizes of approximately 2–3 μm were formed which are slightly above the values of 1–2 μm favorable to prepare

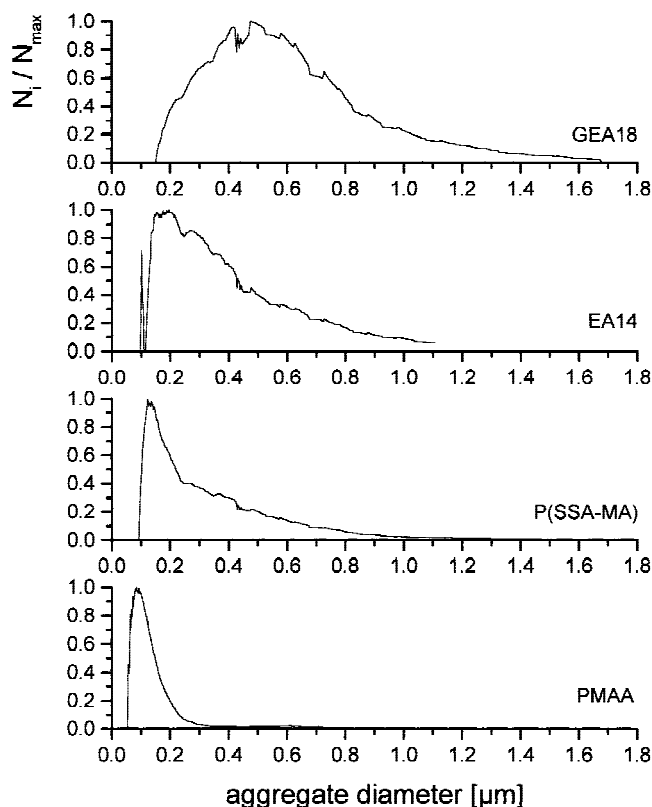


FIG. 2. Aggregate size distributions in suspensions obtained after dispersing the BaTiO_3 powder sample BTM in aqueous polymer (0.5 wt% polymer) solution. (For polymers, see Table I).

TABLE II. Variation in organic auxiliaries for preparing green films.

Formulation	Sample	Dispersant ^a	Binder (PVA) (mg)	Plasticizer (glycerol) 87 wt% in aq. solution (mg)
1	BTM36, BTM39, BTM40		10	120
2	BTM34, BTM37, BTM38	PMAA	20	140

^a5 mg.

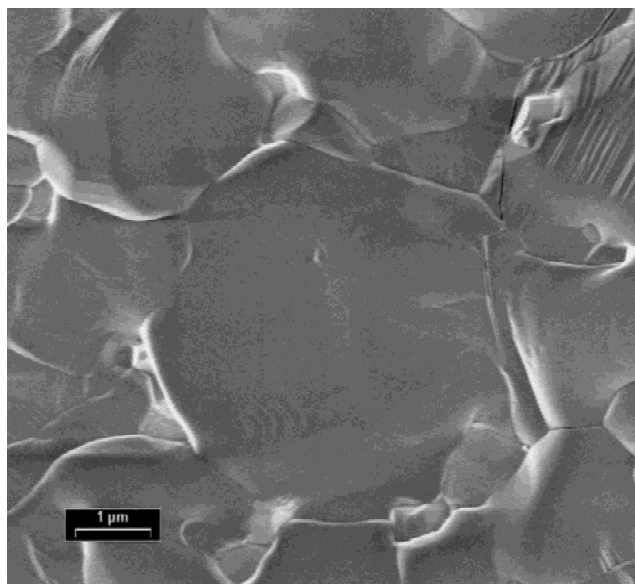


FIG. 3. Surface section of the sintered BaTiO₃ sample BTM36.

ceramics of good dielectric characteristics.^{14,15} A section of a sintered BaTiO₃ surface (sample BTM36) is shown in Fig. 3. All samples exhibited the same microstructure.

These samples were analyzed by XRD and characterized as mainly consisting of tetragonal BaTiO₃. Impurity phases were not found. All of the organic auxiliaries, namely dispersant, binder, and plasticizer, were burned out completely during heating and sintering. The assignment of the tetragonal phase rests on the split off the $\{hk0\}$ and $\{hk0\}$ reflections in x-ray diffraction patterns, whereas the $\{111\}$ peaks remain unsplit indicating that the initial cubic phase was transformed to the tetragonal phase.¹⁶ The XRD pattern of the sample BTM34min sintered under O₂-Ar atmosphere is shown in Fig. 1(b). The significant splitting of $\{200\}/\{002\}$ and $\{301\}/\{103\}$ reflections with respect to the diffractogram in Fig. 1(a) (cubic BaTiO₃) of the as-prepared powder displays this phase transformation. It proceeds by a displacive transition when the sample is cooled.¹⁷ The absolute fraction of tetragonal phase in the BaTiO₃ samples was not determined. But it is evident that only the fraction of the tetragonal ferroelectric phase in the respective samples is responsible for the value of the dielectric constant of the sintered material.¹⁸ It is close to the best values reported in the literature.

Figure 4 represents the variation of the dielectric constant in the vicinity of the Curie temperature (T_C) at 1 kHz, for samples BTM34min and BTM34-36, -38, and -40 to give evidence how sintering affects the properties. In the temperature range 20–85 °C, nearly the same dielectric constant (2250–3250) is achieved for samples prepared with or without using PMAA as a dispersant and sintered under ambient atmosphere. In comparison, sintering a sample (BTM34min) under O₂-Ar

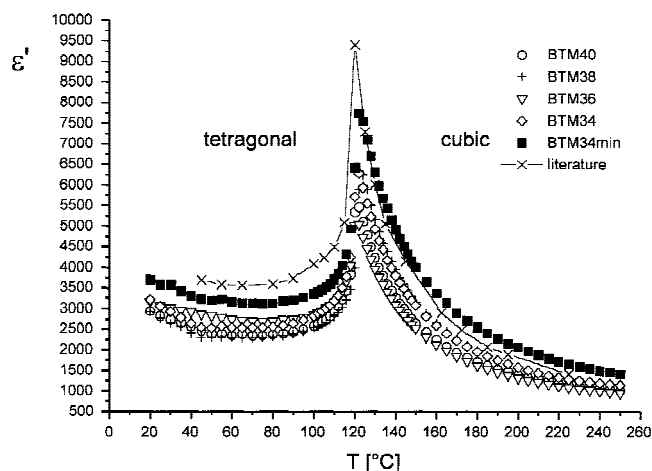


FIG. 4. Temperature dependence of the dielectric constant ϵ' of different ceramic films from sample BTM at a frequency of 1 kHz in comparison to data from Takeuchi *et al.*¹⁸ (—x—).

atmosphere leads to higher values (3250–3750) in the same temperature interval. These data are close to those reported by Takeuchi *et al.*¹⁸

The magnitude of ϵ' is related to the number density of dipoles in the ferroelectric phase,¹⁹ and therefore, to the defect density in the ceramic film.¹⁸ Since the samples differing in magnitude of ϵ' exhibit the same microstructures as seen by SEM, the temperature treatment under O₂-Ar atmosphere must be responsible for the higher dielectric constant of the sample BTM34min. It is assumed that the oxidative atmosphere leads to an increased rate of polymer degradation and pyrolysis and the sinter process starts at lower temperatures. Maximal contact of individual particles becomes possible at earlier stages at the temperature program in comparison to samples sintered under ambient atmosphere. This also means that controlling the atmosphere during sintering helps to optimize the mass transport and gives rise to increased density of the ceramic end product by decreasing the densification temperature.

IV. CONCLUSIONS

BaTiO₃ powders of mean particle sizes of approximately 70 nm were dispersed in aqueous polymer solutions. PMAA turned out to be a good dispersant in the preparation of green films.

The ceramic thin films obtained by sintering the green films under different atmosphere (ambient versus oxygen) differ in their dielectric behavior. Sintering under O₂-Ar atmosphere versus ambient atmosphere gave increased dielectric constants from 2250–3250 to 3250–3750 in the temperature range 20–85 °C (at 1 kHz) while differences in grain growth could not be observed.

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