

Peroxo-oxalate Preparation of Doped Barium Titanate

Sven van der Gijp, Louis Winnubst, and Henk Verweij*

Laboratory of Inorganic Materials Science, Department of Chemical Technology, University of Twente, 7500 AE Enschede, The Netherlands

The peroxo-oxalate complexation method is a method that can be used for the preparation of doped barium titanate. In this paper we focus on $\text{BaTi}_{0.91}\text{Zr}_{0.09}\text{O}_3$, which can be used for discharge capacitors in lamp starters. The preparation method described here is based on the complexation and subsequent precipitation in basic environment of Ba, Ti, and Zr ions with hydrogen peroxide and oxalate. The influence of several process parameters, like precipitation temperature and pH, on powder properties is described. A single-phase perovskite crystal structure is obtained after calcination starting from a chloride precursor solution using a precipitation temperature of 40°C and a pH of 9. Because the peroxo-oxalate process starts with inexpensive chlorides and is performed in air, the peroxo-oxalate process is suitable for the commercial production of doped barium titanate.

I. Introduction

DOPED barium titanate is used in a broad range of electroceramic devices. One example is a pulse-generating device, which can be applied in lamp starters.¹ For this application nonlinear dielectric behavior is required. To obtain the desired nonlinearity the material must possess a steep gradient in the polarization versus electric field hysteresis curve at room temperature. The presence of this steep gradient and significant nonlinearity is correlated with the occurrence of an exceptionally high value of the dielectric constant. Three aspects are important to achieve a high value for the dielectric constant at the Curie temperature:

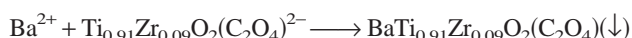
(1) The phase transitions present in barium titanate—cubic–tetragonal, tetragonal–orthorhombic, and orthorhombic–rhombohedral—must overlap (see the plot of the dielectric constant versus temperature in Fig. 1). This overlap of the three phase transitions can be obtained by doping the barium titanate with zirconium,^{2–5} which results in a Curie temperature of approximately 90°C. Consequently below 90°C the material is ferroelectric and has the required type of hysteresis curve.

(2) The ceramic must be chemically homogeneous. The zirconium must be distributed randomly over the material in such a way that the composition is the same throughout the whole ceramic. Local deviations from this composition will lead to a distribution of phase transition temperatures and therefore to a lower value of the maximum dielectric constant.^{6,7}

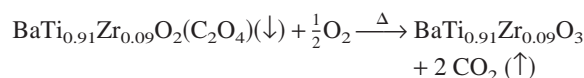
(3) The stress in the final ceramic must be as low as possible. Mechanical stress in the material gives rise to a lower maximum value of the dielectric constant.⁵ The mechanical stress in the material is introduced in the material during cooling after sintering. At the Curie temperature the unit cell of the

10% Zr– BaTiO_3 changes from cubic to rhombohedral, which creates stress. The amount of stress can be reduced when during the thermal processing step domains are formed. When large grains are present, more domains are formed than in ceramics with small grains. Therefore, to obtain a high value for the dielectric constant at the Curie temperature, the grains of the ceramic must be as large as possible and consequently a high sintering temperature is required.

Nowadays, polycrystalline Zr-doped barium titanate for commercial applications is prepared by the mixed-oxide method.^{1,2} The mixed-oxide method is based on solid-state reactions and the powders suffer from low chemical homogeneity.¹⁰ In order to increase the homogeneity of powders and ceramics wet-chemical preparation techniques have to be used instead of mixed oxides.² A suitable wet-chemical preparation technique for Zr-doped BaTiO_3 is the complexation and subsequent precipitation of a titanium peroxo-oxalate species in an aqueous environment.⁸ In this process, barium ions react with a dissolved titanium/zirconium complex:



This complex consists of a peroxo and an oxalate ligand to form an insoluble precipitate. The peroxo ligand originates from the hydrogen peroxide that reacts with hydrolyzed titanium. The precipitate is thermally decomposed by calcination to $\text{BaTi}_{0.91}\text{Zr}_{0.09}\text{O}_3$:



In the present paper the question is addressed whether it is possible to improve the materials performance any further by using a preparation route that will lead to more homogeneous materials. Such a route should obviously include a wet-chemical homogeneous powder preparation process. As indicated before, the peroxo-oxalate route seems very promising for this. The effect of the precipitation temperature, the pH, and the choice of titanium and zirconium precursor on the powder

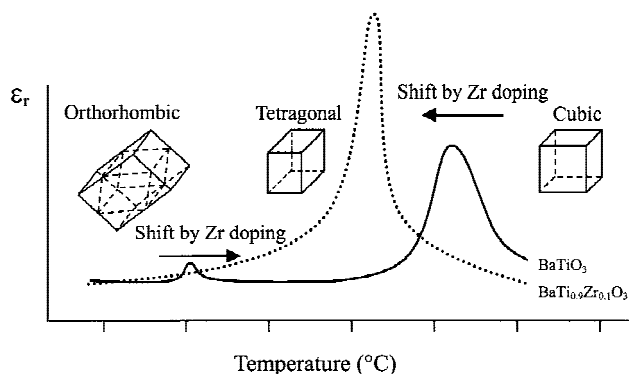


Fig. 1. Schematic diagram of the dielectric properties of pure and Zr-doped barium titanate. The phase transition orthorhombic–rhombohedral (at –90°C in the case of undoped BaTiO_3) is not shown.

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properties, in order to find the optimum process conditions for the preparation of perovskite Zr-doped BaTiO₃, is discussed.

II. Experimental Procedure

Two types of Zr and Ti precursor solutions were used:

(1) In the first system alkoxide precursors, titanium isopropoxide and zirconium *n*-propoxide (70 wt% in 1-propanol), were used.

(2) The second system consisted of titanium oxychloride and zirconium chloride.

The titanium precursor (0.15 mol) and zirconium precursor[†] (0.015 mol) of both systems were poured into aqueous solutions (1 L) of nitric acid (0.2M). These mixed titanium/zirconium solutions were mixed with aqueous solutions (2 L) of barium nitrate, prepared from barium carbonate (0.17 mol) and nitric acid (0.2M). Finally, hydrogen peroxide (0.85 mol) was added to this solution.

Both so-called "precursor" solutions had a total volume of 3.5 L and were added dropwise to a solution of ammonium hydroxide (0.7 mol) and oxalic acid (0.34 mol). The temperature of the ammonium oxalate solution was varied between 10° and 80°C. The total volume after addition was 8 L.

Experiments with alkoxide precursors were conducted in a pH range of 4 to 10, obtained by adding the appropriate amount of ammonium hydroxide to an aqueous solution of oxalic acid. When the pH changed during addition, the pH was adjusted by the addition of small amounts of ammonium hydroxide. Except for this experiment with different pH values, all other experiments were conducted at pH 9. To ensure complete complexation and precipitation, after addition the solution was stirred for 2 h at the precipitation temperature. The precipitate was separated from the solution by filtration and washed with water to remove chloride ions, washed with ethyl acetate to decrease the agglomerate strength, and finally dried at 150°C, ball-milled in 2-propanol, and calcined at 900°C for 5 h, with a heating and cooling rate of 5°C·min⁻¹.

Ceramics were obtained by pre-pressing uniaxially at 80 MPa and subsequently isostatically pressing at 400 MPa. All compacts were sintered at 1400°C in air for 5 h, with a heating rate of 2°C·min⁻¹ and a cooling rate of 4°C·min⁻¹.

The concentration of the metal ions in solution was determined prior to mixing. The barium concentration was determined by titration with a standard EDTA solution, using methyl thymol blue as an indicator.⁹ The concentration of titanium and zirconium in separate solutions was determined by thermogravimetric analysis after thermal decomposition of the precursor solution.

Crystal structures were revealed by XRD, using a Philips PW 1710 with filtered CuKα1, λ = 1.4508 Å. The chemical composition of the calcined powders was measured by XRF using an X-ray spectrometer (Philips PW 1480/10).

The particle size distribution was measured with a Microtrac X-100 in a diluted aqueous system (Leeds and Northrup). For data analysis it was assumed that the powders were completely reflecting and spherical. The morphology of the powder was studied with field emission scanning electron microscopy (Hytachi, type S800).

The microstructure of the polished ceramic samples was revealed by thermal etching in a nitrogen atmosphere at 1370°C, followed by sputtering with gold. The microstructure was studied with scanning electron microscopy (Jeol, JSM 8500).

Nonisothermal densification was studied with a Netzsch 410 dilatometer. The heating rate was 2°C·min⁻¹, the cooling rate 4°C·min⁻¹, and the holding time 3 h at a temperature of

1400°C. Density measurements were performed with the Archimedes technique, using mercury.

III. Results and Discussion

(1) Influence of pH

The effect of pH on complexation and precipitation was studied by varying the pH in the range of 4 to 10 at room temperature using titanium alkoxide and zirconium alkoxide as precursors. In the literature high and low pH are used in, respectively, the peroxy and the oxalate precipitation processes for the preparation of barium titanate.^{11,12} In Fig. 2 it is apparent that the amount of second phase decreases drastically when the pH is increased. XRD shows no difference between the calcined powders prepared at pH 8.5 or 10. The second phases as found by XRD for the whole pH range are BaTi₂O₅ and BaCO₃. Next to the amount of second phase in the calcined powders the color of the solution after precipitation also changes. At low pH the solution is red. This color diminishes with increasing pH of the solution after addition, and the solution eventually becomes colorless at pH 8.5 and 10. Since a small amount of titanium peroxy complex in aqueous solution results in a red color,⁹ the change in color of the filtrate from red at pH 4.5 to colorless at pH 8.5 and 10 indicates that at low pH titanium-peroxy complexes remain dissolved, whereas Ti_{0.91}Zr_{0.09}(O₂)(C₂O₄)²⁻ is formed at high pH,⁸ which is thermally more stable than the complex without oxalate.¹³ At low pH another complex, Ti(O₂)OH⁺, is formed which does react with barium to give an insoluble complex.¹⁰ Therefore, the titanium complex is subject to condensation, which eventually results in the formation of an inhomogeneous precipitate. Because of the presence of the peroxy ligand, the titanium complex is in such a form that the titanium-peroxy complex as well as the barium ions will remain in solution at low pH.

Note that the difference in complexation and precipitation behavior between the peroxy-oxalate process and the commercial oxalate process, which is used for the preparation of undoped barium titanate, can be explained by the presence of the peroxy ligand. The structure of the precipitating complex in the oxalate method, BaTiO(C₂O₄)₂·4H₂O, is different from that of the precipitating complex in the peroxy-oxalate method, BaTi_{0.91}Zr_{0.09}O₂(C₂O₄)·3H₂O. Because of this change in complex structure the precipitation behavior of the titanium oxalate complexes changes significantly.⁸

(2) Influence of Precipitation Temperature with Alkoxide Precursors

To study the effect of temperature on the complexation properties of the titanium peroxy-oxalate complex, precipitation experiments were performed in a temperature range from 0° to 80°C at pH 9. In Fig. 3 the XRD results are given for calcined powders, prepared by precipitation at different precipitation temperatures. It is clear that precipitation at 60°C leads to a

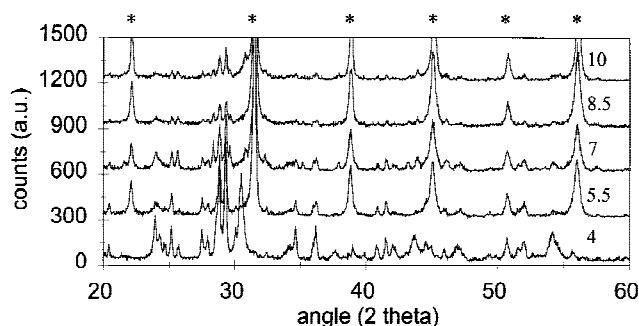


Fig. 2. XRD of calcined powders prepared from an alkoxide precursor at different pHs, precipitation temperature 20°C. * indicates perovskite BaTiO₃.

[†]Titanium isopropoxide and zirconium *n*-propoxide, p.a. grade, were obtained from Aldrich, Steinheim, Germany; all other chemicals, at least p.a. grade, were obtained from Merck, Darmstadt, Germany.

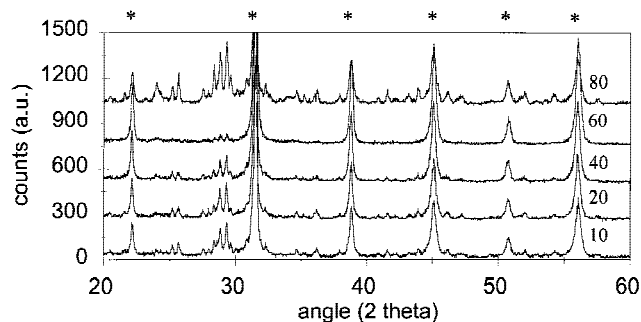


Fig. 3. XRD results of calcined powders prepared from an alkoxide precursor at pH 9 at different precipitation temperatures. * indicates perovskite BaTiO_3 phase.

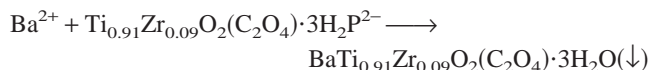
powder with the smallest amount of second phase. At a precipitation temperature of 80°C considerable amounts of second phases, BaTi_2O_5 and BaCO_3 are formed.

To explain why second phase occurs, it is necessary to describe the various processes, which play a role during the peroxo-oxalate process:

(1) Before addition to the aqueous ammonium oxalate solution, at pH 3 (slow) hydrolysis of the zirconium and the titanium precursor (alkoxide or oxychloride) occurs. It is expected that BaCO_3 is dissolved directly as Ba^{2+} , after the addition of nitric acid.

(2) Complexation of the titanium and zirconium species with hydrogen peroxide will occur after hydrolysis. At low pH complexes such as $\text{Ti}(\text{O}_2)\text{OH}^+$ are present in solution.¹⁰

(3) The complex structure changes by addition of the precursor solution to the ammonium oxalate solution. Because of the change in pH from 3 to 9 and the presence of hydrogen peroxide and oxalate, the structure of the complex changes to $\text{Ti}_{0.91}\text{Zr}_{0.09}\text{O}_2(\text{C}_2\text{O}_4)^{2-}$.⁸ Therefore, the formation of the precipitating complex can be described as follows:



Next to the processes described above, a side reaction may also occur, condensation of the zirconium and titanium components. Condensation reactions occur at both high and low pH. Note that the rate of condensation is much faster at high pH values. The precipitation mechanism depends on the pH; nevertheless, eventually the same final product is obtained, $\text{TiO}_3(\text{H}_2\text{O})_x$.¹¹ Condensation is an undesired side reaction, which leads to titanium-rich phases and therefore to inhomogeneities in the calcined powder and ceramic. It is expected that for zirconium a condensation mechanism occurs similar to titanium. In conclusion, to obtain a homogeneous powder condensation should be prevented.

The hydrolysis of titanium and zirconium isopropoxide proceeds rather slowly. Directly after addition of the precursor to

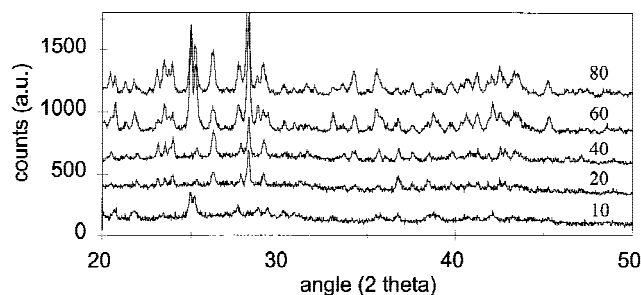


Fig. 4. XRD results of uncalcined powder prepared from a chloride precursor at different precipitation temperatures.

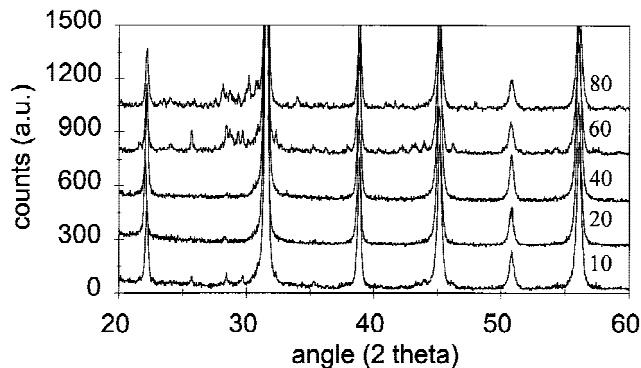


Fig. 5. XRD results of calcined powders prepared from a chloride precursor at pH 9 at different precipitation temperatures.

water a white precipitate is formed which dissolves very gradually. When the precursor solution is added to the ammonium oxalate solution and consequently the pH is raised from 3 to 9, the structure of the titanium-peroxo complex changes as described above. When hydrolysis is incomplete after addition of the precursor to the ammonium oxalate solution, species other than $\text{Ti}_{0.91}\text{Zr}_{0.09}\text{O}_2(\text{C}_2\text{O}_4)^{2-}$ will be formed, giving rise to second-phase formation. This effect may arise when hydrolysis of titanium is not complete before addition to the ammonium oxalate solution. To extend the time before adding the precursor solution to the ammonium oxalate solution might result in condensation reactions in the precursor solution.

Another explanation for the formation of second phases at low temperatures might be an incomplete complexation with oxalate and hydrogen peroxide. The species formed by incomplete hydrolysis or incomplete complexation give rise to second-phase formation.

At higher precipitation temperatures condensation will occur. At 80°C the precursors are fully hydrolyzed, but now because of the high precipitation temperatures, more and faster condensation will take place. Condensation processes lead to the formation of second phases.¹¹ In this case in Fig. 3 both a titanium-rich and a barium-rich phase (BaCO_3 , most intense peak at $24^\circ 2\theta$) are formed.

Precipitation at 60°C starting with alkoxide precursors results in a calcined powder with the lowest amount of second phases. Diminishing second-phase formation is achieved by looking for a compromise between incomplete complexation and rapid condensation at high temperatures. In the case of alkoxide precursors second-phase formation cannot be avoided completely.

(3) Influence of Precipitation Temperature with Chloride Precursors

In Fig. 4, XRD spectra are given of the uncalcined powders, prepared with chloride precursors at pH 9. It is apparent that some crystallinity is present before calcination. The intensity and therefore the amount of crystalline phase increases with increasing precipitation temperature. The XRD pattern of the main phase present in the uncalcined powders is comparable to that of barium oxalate [18-0203],[‡] with the most intense peak at $25^\circ 2\theta$. The XRD spectra of the precipitates prepared at 10° and 60°C show another phase, which is similar to barium oxalate hydrate [20-0134]. Note that for all of the signals no exact fit with reference spectra could be made. The presence of a species similar to barium oxalate is obvious for all precipitation temperatures. The reason that in two cases a different hydrate is formed is not clear; small variations in the drying step may account for this.

Figure 5 shows the diffraction data of the calcined precipi-

[‡]Numbering, according to ICDD.

tates prepared in a temperature range of 10° to 80°C. It is clearly visible that no or a very small amount of a second phase is formed during precipitation at 20° and 40°C. It is also visible that the amount of second phases formed during precipitation at 60° and 80°C is higher compared to the amount of second phases found for the calcined powder prepared with a precipitation temperature of 10°C.

The second phases present in the calcined powders mainly consist of BaTi₂O₅ and BaCO₃, the same phases as observed when an alkoxide precursor is used. The mechanism of formation of the second phases is the same as in the case of the alkoxide precursor. Again at high temperatures the formation of second phases can mainly be attributed to condensation processes. At 10°C either the starting chloride is not fully hydrolyzed or the ligand exchange of the peroxo ligand with the oxalate is incomplete. Both mechanisms will lead to the formation of second phases.

In Table I the green and final densities are given for compacts prepared at different precipitation temperatures. The green density of the compacts prepared at higher temperature is slightly higher than the green density of the compacts prepared below 40°C. The final density of the compact prepared with a precipitation temperature of 40°C has the highest density (98%). This was expected since the precipitate has the smallest particles and the calcined powder prepared at a precipitation temperature of 40°C has the lowest content of second phase (see Figs. 5 and 7).

XRF indicates that the hydrolysis and condensation reactions have an influence only on the second-phase formation of the powder but do not affect the final composition of the calcined powder (see Table II). Precipitation at a temperature of 20° to 40°C results in the most homogeneous powder.

(4) Influence of Precursor Type

The advantage of the use of alkoxide instead of chlorides as a precursor is that only organic matter has to be removed from the precipitate, which can easily be done by calcination. The presence of chloride ions in the precipitate will result in the formation of a BaCl₂ liquid phase during sintering.¹⁰ To prevent this impurity effect, chloride ions have to be removed completely, which is not possible by calcination but which has to be performed by washing.

In Fig. 6 the XRD spectra are given of powders obtained by calcination of the precipitates formed with either chloride precursors or alkoxide precursors. Both samples are prepared under the same reaction conditions, i.e., precipitation at 20°C and at pH 9. It is clearly visible that the powder prepared with the alkoxide precursor contains some second phase, BaTi₂O₅ (see also Figs. 4 and 5). Clearly smaller amounts of second phases are formed in the case of chlorides than in powders prepared out of alkoxide precursors. XRF indicates that the calcined powders prepared of different precursors have the same composition. Therefore, it can be concluded that for both systems complete complexation and precipitation occurs. In the case of the use of chloride precursors this precipitate and also the calcined powder are more homogeneous.

Table I. Density Before and After Sintering of Compacts Made from Powder Prepared at Different Precipitation Temperatures Using Chloride Precursors at pH 9[†]

Precipitation temp (°C)	Green density (%)	Final density (%)
10	56	92
20	57	94
40	58	98
60	60	86
80	59	78

[†]Sintering conditions: heating and cooling rate, 2°C·min⁻¹; sintering temperature, 1400°C; time, 5 h. Densities are relative and based on the theoretical density of BaTiO₃ (6.02 g·cm⁻³).

Table II. Molar Ratios of Elements as Measured with XRF Corresponding to Various Processing Steps[†]

Process step	Ba	Ti	Zr	(Ti + Zr)/Ba
Solution	1.000	0.909	0.095	1.003
After precipitation	1.000	0.912	0.091	1.002
Washed	1.000	0.913	0.092	1.004
After filtration	1.000	0.913	0.0900	1.003

[†]After each sample was taken from process, samples were calcined at 1000°C. Process parameters: precipitation temperature, 20°C; chloride precursor; pH 9.

The difference in the amount of second phases can be explained by the difference in the hydrolysis rate of both precursors. Titanium chloride hydrolyzes immediately in water.¹¹ During addition of the alkoxides to diluted nitric acid it is clearly visible that the titanium alkoxide and zirconium alkoxide hydrolysis is much slower than with the analogous precursors. Consequently, complexation with barium, hydrogen peroxide, and oxalic acid will take place more slowly and complexation may be incomplete, causing the titanium species in solution to be subject to condensation longer.

(5) General

From the results described above, it can be concluded that in the peroxo-oxalate process chloride precursors have to be used at pH 9 and a temperature of approximately 20° to 40°C. To ensure that the processing steps under these conditions had no effect on the final stoichiometry of the powder, the concentration of the elements was measured after each separate processing step (see Table II). No variation in the concentration ratio could be observed during the various processing steps.

A change in addition speed of the precursor solution to the ammonium oxalate solution did not lead to variations in the phase composition nor to the formation of second phases, even when the precursor solution was poured directly into the ammonium oxalate solution.

After calcination the powders were wet-milled in 2-propanol. In the literature it is known that during milling leaching of barium might take place.¹⁴ XRF showed that the change in concentration due to milling remained within the error of the measuring technique.

Another important parameter in the peroxo-oxalate process is the amount of hydrogen peroxide in solution. Duvigneaud *et al.*¹⁵ have reported that for a comparable homogeneous precipitation (without oxalate) of pure barium titanate the amount of hydrogen peroxide needs to be very high (H₂O₂:Ba = 40:1) to ensure complete precipitation of all the barium. We found that when the ratio of hydrogen peroxide to barium was changed from 40:1 to 5:1, no change in the composition was found with XRF.

The particle size of the dried complexes decreased with increasing precipitation temperature. In Fig. 7 the differences in

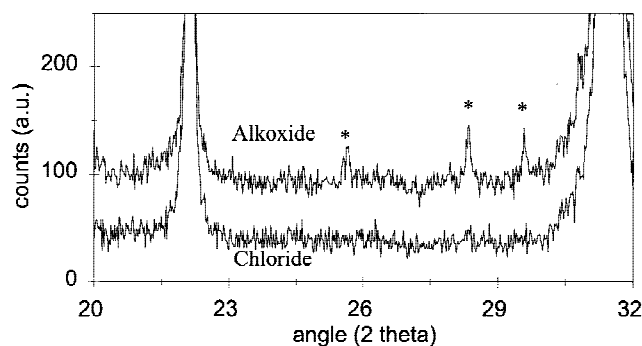


Fig. 6. XRD of calcined powders prepared from a chloride precursor and alkoxide precursor, precipitation temperature 20°C, chloride precursor. * indicates second phases.

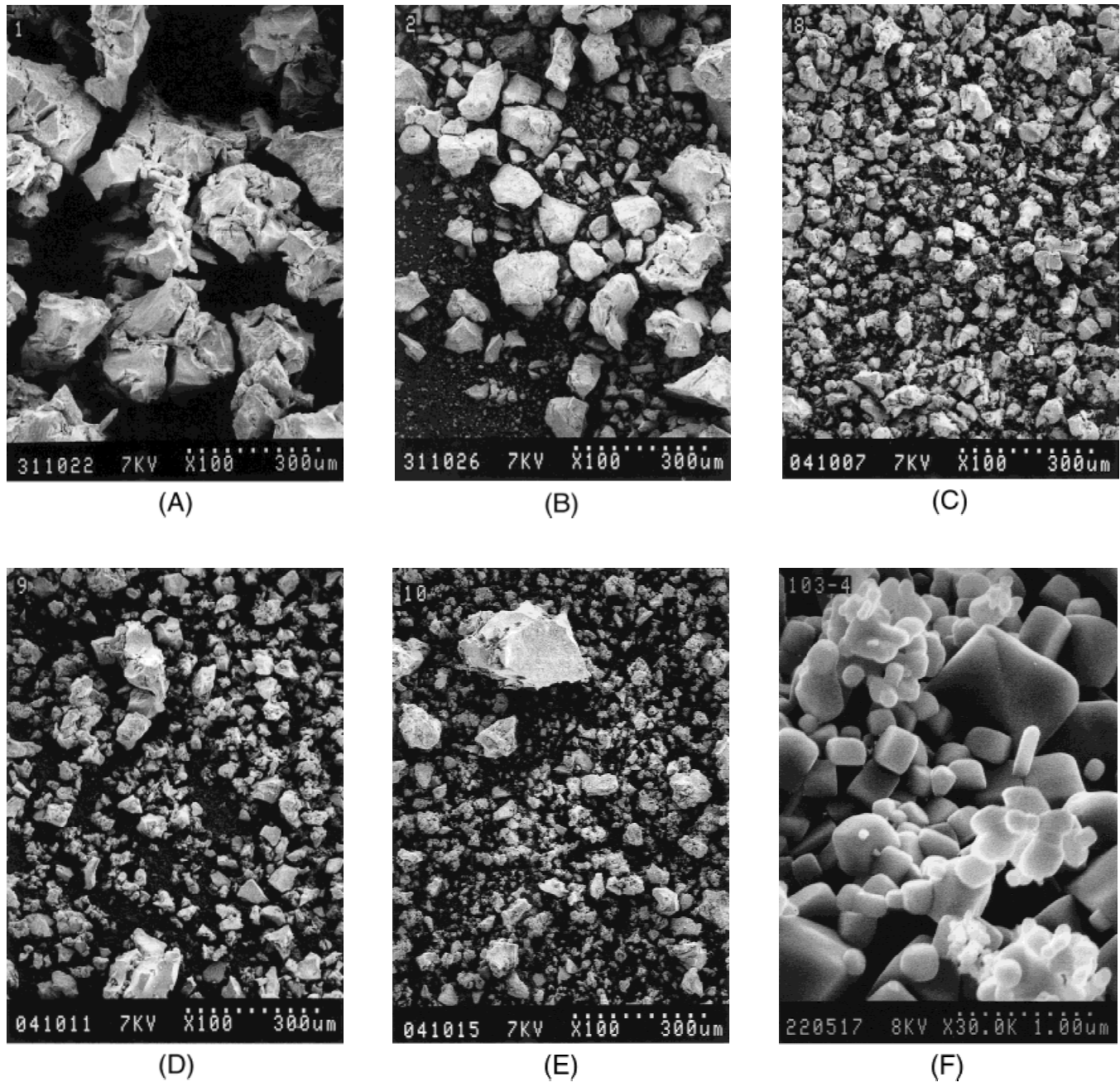


Fig. 7. Micrographs of calcined powders prepared at different precipitation temperatures, chloride precursor and pH 9: (A) 10°, (B) 20°, (C) 40°, (D) 60°, (E) 80°C, (F) detail of powder prepared at 60°C.

particle size of various dried precipitates are shown. Powders prepared above 40°C consisted of smaller aggregates than powders prepared below this temperature; however, the primary particle size as measured by SEM was independent of the precipitation temperature and was established to be around 0.2 μm . The amount of crystalline phase increased with precipitation temperature, as shown in Fig. 4. The reason that the aggregate size is related to the precipitation temperature is not clearly understood.

In Fig. 8 the densification curve of a representative sample is shown (chloride precursor, precipitated at 20°C). Sintering starts at 1180°C and is complete at approximately 1300°C. During sintering the density increases from 56% to 98%. The microstructure of the sintered compact is shown in Fig. 9. In this micrograph large grains are visible with an average grain size of 160 μm . The ceramic has a maximum relative dielectric

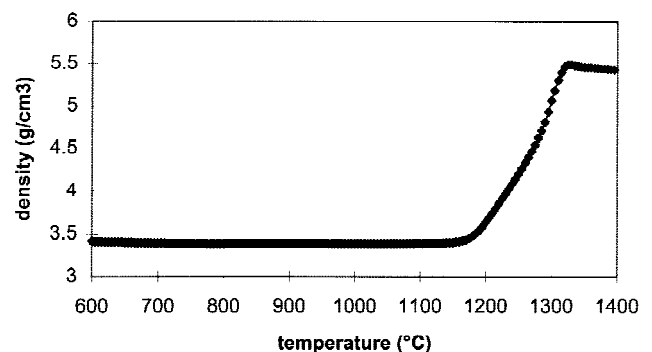


Fig. 8. Densification curve of a compact prepared from chloride precursor at pH 9 and 20°C.

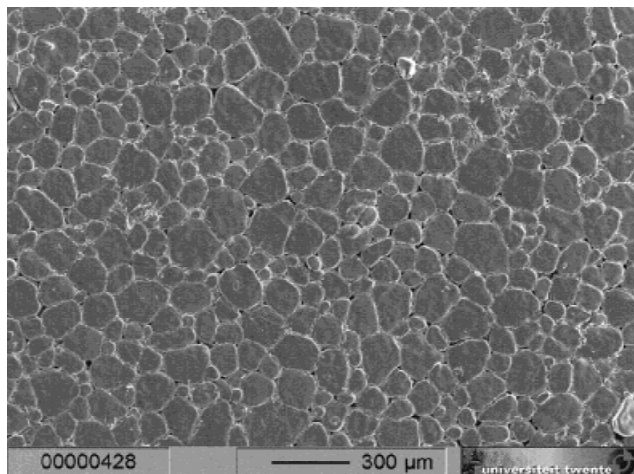


Fig. 9. Microstructure of ceramic prepared with the peroxy-oxalate method.

constant at the Curie temperature of 88°C of approximately 28 000. This is comparable to values found by Neirman for ceramics prepared from commercial powders.² Unfortunately the data of Neirman are not comparable to our data.

The method as described in this paper might provide a starting point for the commercial preparation of barium titanate ceramics. For industrial application of wet-chemical processes several requirements have to be met:

(1) First of all, the reaction atmosphere must be preferably in air. However, normally air is not used because it contains carbon dioxide, which can easily react with barium to form the undesired product barium carbonate, leading to unwanted second-phase formation in the final stages of the process. Therefore, in the majority of the wet-chemical processes for the preparation of barium titanate a nitrogen atmosphere is used. The peroxy-oxalate method as described in this paper is, however, a process that can easily be conducted in air and results in the formation of a single-phase perovskite material.

(2) A second requirement for industrially feasible processes is the use of inexpensive starting materials such as (oxy)chlorides. Alkoxide precursors are too expensive and in the case of barium also moisture sensitive. With the peroxy-oxalate process the use of chloride precursors is very possible and preferred above alkoxide precursors since they lead to a lower amount of second phase in the material.

The peroxy-oxalate process meets both requirements for industrial application. It can also be interesting to use this process for the commercial preparation of inorganic powders with different compositions, e.g., powder for the manufacturing of multilayer ceramic capacitors.

The chemical homogeneity of the ceramics prepared by the oxalate method is only slightly different from a commercially hydrothermal prepared powder and a mixed-oxide prepared powder (data concerning the homogeneity are described elsewhere¹⁶). The use of the peroxy-oxalate method still does not offer special advantages in this respect but may prove to be beneficial compared to other wet-chemical processes for the preparation of ceramics for other purposes.

It seems also very promising to perform the peroxy-oxalate process in combination with emulsion processing. The control of the phase composition can then be combined with the well-defined morphology of powders obtained with emulsion processing.

IV. Conclusions

For the peroxy-oxalate method as described in this paper, the reaction parameters like precursor choice, precipitation temperature, and pH have a strong influence on the crystal structure and homogeneity of the calcined powder. To ensure the formation of a homogeneous powder the peroxy-oxalate process has to be conducted at pH 9 and started with chloride precursors. The pH during precipitation needs to exceed 9, because only at high pH values is a complex formed which precipitates stoichiometrically with barium. The use of alkoxide precursors is not recommended because their use will lead to more second-phase formation. A precipitation temperature of 40°C is optimal, since at this temperature the lowest amount of second phase is formed. At higher temperatures condensation of hydrolyzed precursors occurs, leading to unwanted second-phase formation later on.

The peroxy-oxalate method conducted at pH 9, 40°C and starting with a chloride precursor results in a stoichiometric, sinterable powder of which the corresponding ceramic has a high dielectric constant of 28 000 at the Curie temperature of 88°C. The process is interesting because dopants can be introduced easily and stoichiometrically. The starting materials are inexpensive, and finally the process does not suffer from barium carbonate formation and can therefore be performed in air without problems.

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