Preparation of homogeneously-doped barium titanate

Sven van der Gijp

Gijp, Sven van der

Preparation of homogeneously-doped barium titanate

PREPARATION OF HOMOGENEOUSLY-DOPED BARIUM TITANATE

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
prof. dr. F.A. van Vught,
volgens besluit van het College voor Promoties
in het openbaar te verdedigen
op donderdag 10 september 1998 te 13.15 uur.

door

Sven van der Gijp

geboren op 27 maart 1971

te Amstelveen

dit proefschrift is goedgekeurd door de promotor

prof. dr. ir. H. Verweij

en de assistent promotor

dr. A.J.A. Winnubst

Summary

Doped barium titanate is used frequently in several types of electrical devices. The electrical behaviour of barium titanate ceramics strongly depend on the composition and the microstructure. In this thesis mainly the application of zirconium doped barium titanate as a pulse-generating device is described. Next to this also the application of barium titanate in multilayer ceramic capacitors is briefly discussed. Finally the preparation of homogeneously doped barium titanate powder is described as well as the microstructure and the related properties of the ceramic.

In *chapter 1* the ferroelectric behaviour of barium titanate as well as the influence of dopants on the dielectric behaviour and more specific on the position of the Curie-temperature are described. The physical background on the use of barium titanate for application in lamp starters and in multilayer ceramic capacitors is also discussed. For the application in a lamp starter it is essential that the ceramic is chemically homogeneous and consists of large grains. For application in the multilayer capacitor the particle size is the determining factor.

In *chapter 2* a survey of the preparation method for (doped) barium titanate which has been published previously in literature is given. A subdivision in preparation method is made in complexation, precipitation, sol-gel and dispersion techniques. For each technique a number of different preparation methods are given. In this survey emphasis is put on the chemical background of the process as well as the morphology and sinteractivity of the resulting powders. Several of these techniques are tested. Precipitation and complexation-precipitation seem the most suitable techniques for the commercial production of doped barium titanate, because cheap precursors can be used and moreover, because no or only a low amount of organic molecules are used and because the processes can be conducted in an aqueous environment without too many complicated processing steps,.

The preparation of barium titanate with the oxalate and peroxide method is described extensively in literature, however the preparation of doped barium titanate is not. When oxalate is added to the peroxide process, the so-called peroxo-oxalate process is formed. In *chapter 3* it is described that the addition of oxalate results in an improvement of the morphology of the powder as well as the prevention of second phase for-

mation. The improved powder properties are likely to be due to the formation of $BaTi_{0.91}Zr_{0.09}O_2(C_2O_4)\cdot3H_2O$ during the complexation-precipitation stage of the process. The structure of this complex is confirmed by a study on the thermal decomposition behaviour.

In *chapter 4* the peroxo-oxalate method is studied in closer detail. To prepare a single-phase powder with a small grain size it is required to start the peroxide process with a chloride salt as precursor. Due to the slow hydrolysis rate, the use of alkoxides as precursors results in the formation of undesired second phases. Next to the hydrolysis rate, the precipitation temperature is of great influence to the particle size also and second phase formation. A precipitation temperature of 40°C, combined with the use of the chloride precursor, will lead to the best results. It is further required to keep the acidity of the ammonium oxalate solution above pH = 9.

The particle size and the degree of aggregation of powders produced by the peroxo-oxalate method can be reduced further. A method that seems suitable to do so is the so-called homogeneous precipitation. In *chapter 5* three different methods for homogeneous precipitation are discussed. First the esterification is described, in which by means of an esterification reaction water is generated, which reacts with barium and titanium precursors in an alcoholic environment. Due to difference in hydrolysis rate between the barium and titanium precursor this method results in the formation of undesired second phases. Secondly the complexation method is described, in which a Ba-EDTA complex is thermally decomposed. This method results in a powder with spherical aggregates of approximately 1 µm in diameter. Finally the urea method is discussed, in which the pH of an aqueous solution is raised by a hydrolysis reaction of urea, which results in the formation of a precipitate. Unfortunately, it is not possible to precipitate barium and titanium simultaneously. All three powders have a reasonably well-defined morphology but still the degree of aggregation can be reduced further. For all three methods a large titanium excess is found with XRF measurements. This excess was the largest in case of the urea method. More development is required in order to make homogeneous precipitation a suitable method for the preparation of barium titanate.

As mentioned before, the homogeneity of the ceramic is important when barium titanate is applied as a pulse-generating device. Little is known in literature about the determination of homogeneity. In *chapter 6*, therefore, a number of techniques are discussed and compared, for example Auger, SEM-EDX and EPMA which can be used

for the determination of the chemical homogeneity of the three powders and their derived ceramics. A hydrothermally prepared powder obtained from Sakai, a peroxo-oxalate prepared powder and a mixed oxide prepared powder are tested. The latter is prepared by a solid state reaction. No or only a small difference in chemical homogeneity between the various ceramics could be found and hence no relation could be found between the homogeneity of ceramics and the homogeneity of powders. This can easily be explained by the occurrence of diffusion at the high temperature used for sintering. SEM-EDX measurements indicate that the deviation in zirconia concentration in the commercial Sakai powder is the largest. To measure the homogeneity of ceramics, Auger spectroscopy seems the best method because, the concentration can be measured locally due to the small spot size.

In *chapter 7* the effect of mechanical stress and chemical homogeneity on the dielectric properties of zirconia doped barium titanate is described. To reduce the level of stress, large grains which can be formed with slow heating rates are required. However, it seems that a high sintering temperature has more influence on the value of the maximum dielectric constant than on the grain size. Moreover, no relation between the value of the dielectric maximum and the grain size could be found. Nevertheless, a relation between the height of the maximum constant and the position of the Curie-temperature can be found.

Finally, in *chapter 8* perspectives for the research on lamp starters and multilayer capacitor devices are given. For the use of multilayer capacitors, emulsion technology seems very promising, because the resulting fine particles in the solution can directly be used in a tape casting process. Next, a study for the preparation of multilayer capacitors without shaping techniques seems interesting. For the application in lamp starters, the control of composition and the powder morphology seem very important. It is necessary to find the main reason for the lowering of the maximum dielectric constant. Finally it is essential that a standard procedure for the analysis of homogeneity data is developed.

IV

Samenvatting

Gedoteerd bariumtitanaat wordt vanwege de ferro-elektrische eigenschappen veel toegepast in allerlei elektrische schakelingen. Het elektrische gedrag van materialen gebaseerd op bariumtitanaat is sterk afhankelijk van de samenstelling en microstructuur. In dit proefschrift wordt voornamelijk aandacht besteed aan de toepassing van zirconium gedoteerd bariumtitanaat als puls genererend onderdeel in lamp starters. Daarnaast wordt ook de toepassing in multilaag keramische condensatoren zijdelings belicht. Tevens wordt aandacht besteed aan de bereiding van homogeen gedoteerd bariumtitanaat poeder, de microstructuur en eigenschappen van het keramiek, dat daarvan gemaakt kan worden.

In h*oofdstuk 1* wordt het ferro-elektrische gedrag van bariumtitanaat en de invloed van doteringen op de diëlektrische eigenschappen en meer specifiek op de ligging van de Curie-temperatuur beschreven. Ook worden de fysische achtergronden van de lamp starter en multilaag condensator beschreven. Bij toepassing in lamp starters is het van belang dat het keramiek chemisch homogeen is en bestaat uit grote korrels. Bij toepassing in een multilaag condensator is de morfologie van het poeder de meest belangrijke factor.

In *hoofdstuk 2* wordt een overzicht gegeven van in literatuur beschreven bereidingsmethoden van (gedoteerd) bariumtitanaat. Daar wordt een onderverdeling gemaakt in complexatie-, precipitatie-, sol-gel- en dispersiemethoden. Bij elke methode wordt een aantal verschillende bereidingstechnieken gegeven. Daarbij ligt de nadruk op de chemische aspecten van het proces, alsmede de morfologie en sinteractiviteit van het gevormde poeder. Enkele methodes zijn verder nagewerkt. De precipitatie- en complexatie-precipitatietechnieken lijken het meest geschikt voor de commerciële bereiding van gedoteerd bariumtitanaat. Beide technieken gaan uit van goedkope grondstoffen en gebruiken weinig of geen organische verbindingen voor bijvoorbeeld complexatie. Bovendien kunnen beide methodes in waterig milieu uitgevoerd worden en zijn er geen complexe processtappen noodzakelijk.

De oxalaat en de peroxide methodes zijn beide reeds in de literatuur bekend, maar niet voor de bereiding van gedoteerd bariumtitanaat. Indien er oxalaat wordt toegevoegd tijdens het peroxide proces wordt het aldus ontstane proces de peroxo-oxalaatmethode

genoemd. In *hoofdstuk 3* wordt beschreven dat deze toevoeging van oxalaat als voordeel heeft dat tweede fasevorming in het poeder vermeden wordt, alsmede dat de poedermorfologie verbeterd wordt. De verbeterde eigenschappen zijn zeer waarschijnlijk veroorzaakt, door het peroxo-oxalaatcomplex $BaTi_{0.91}Zr_{0.09}O_2(C_2O_4)\cdot 3H_2O$ dat tijdens de complexatie-precipitatie stap in het proces aanwezig is. De samenstelling van dit complex wordt bevestigd door middel van een studie naar het thermisch ontledingsgedrag van dit complex.

In *hoofdstuk 4* wordt de peroxo-oxalaat methode nader bestudeerd. Om een éénfasig poeder te maken met een kleine deeltjesgrootte is het van belang om het peroxo-oxalaat proces te starten met een chloridezout. Bij het gebruik van alkoxides onstaat een tweede fase in het poeder vanwege de geringe hydrolysesnelheid. Tevens blijkt dat de precipitatietemperatuur een belangrijke invloed heeft op tweede fasevorming en op de deeltjesgrootte van het poeder. Een precipitatietemperatuur van 40°C in combinatie met een chlorideprecursor levert de beste resultaten op. Verder is het noodzakelijk om tijdens het proces de zuurgraad van de oxalaatoplossing boven de pH = 9 te houden.

De aggregatiegraad en de deeltjesgrootte van het poeder, zoals gevormd met het peroxo-oxalaatproces zou nog verlaagd kunnen worden. Een methode die hiervoor geschikt lijkt is de zogenaamde homogene precipitatie. In *hoofdstuk 5* worden drie verschillende homogene precipitatiemethoden beschreven. De eerste is de esterificatiemethode, waarin door middel van een esterificatie reactie water gevormd wordt, dat reageert met barium- en titaanalkoxides in een alcoholisch milieu. Deze methode levert ongewenste tweede fasen in het poeder op, doordat de hydrolyse snelheden van de barium- en titaniumprecursors te verschillend zijn. Ten tweede is er de complexatiemethode, waarbij een Ba-EDTA complex thermisch ontleed wordt. Deze methode geeft mooie ronde aggregaten van ongeveer 1 µm. Tenslotte wordt de ureummethode beschreven. Deze methode is gebaseerd op de hydrolyse van ureum, waardoor de zuurgraad van de oplossing daalt, wat precipitatie tot gevolg heeft. Bij deze methode is het lastig om barium en titanium tegelijkertijd te laten reageren. Alle drie de methodes resulteren in een poeder met een goede morfologie, hoewel de aggregatiegraad nog steeds verlaagd kan worden. Voor alle drie de methoden wordt echter ook een grote overmaat titanium in het poeder gevonden, welke de grootste is bij de ureummethode. Meer ontwikkeling is noodzakelijk om de homogene precipitatie tot een geschikte methode te maken voor de bereiding van bariumtitanaat.

Zoals eerder aangegeven is de homogeniteit van keramiek erg belangrijk als het wordt gebruikt voor in een lampstarter. Over de bepaling van homogeniteit is in de literatuur weinig bekend. In *hoofdstuk 6* wordt daarom een aantal technieken beschreven en getest voor de karakterisering van de chemische homogeniteit van bariumtitanaat-keramiek en -poeders, bijvoorbeeld SEM-EDX, EPMA en Auger. Het betreft een hydrothermaal bereid commercieel poeder (Sakai), een peroxo-oxalaatpoeder en een mixed-oxidepoeder. Het laatste is bereid door middel van een vaste stof poederreactie. Voor de eigenschappen van het keramiek kan weinig of geen verschil gevonden worden met betrekking tot het gebruikte poeder. Dit kan eenvoudig verklaard worden door het optreden van diffusie als gevolg van de hoge sintertemperatuur. Uit SEM-EDX metingen blijkt dat de variatie in zirconiumconcentratie het grootst is voor het Sakai poeder. Voor homogeniteits metingen lijkt Auger de beste methode, omdat vanwege de kleine bundelgrootte heel lokaal de intensiteiten gemeten kunnen worden.

In *hoofdstuk 7* wordt het effect van mechanische spanning en chemische homogeniteit op de diëlektrische eigenschappen van zirconium gedoteerd bariumtitanaat beschreven. Om de spanning in het keramiek te reduceren zijn grote korrels noodzakelijk. De grote korrels kunnen worden gevormd door een lage opwarmsnelheid tijdens sinteren. Het blijkt echter dat een hoge sintertemperatuur meer invloed heeft op de waarde van de maximale diëlektrische constante dan de korrelgrootte. Bovendien kan in het geval van mixed-oxidekeramiek, geen verband worden gevonden tussen korrelgrootte en de waarde van de maximale diëlektrische constante bij de Curie-temperatuur. Wel wordt experimenteel een relatie vastgesteld tussen de maximale diëlektrische constante en de ligging van de Curie-temperatuur.

In *Hoofdstuk 8*, tenslotte, worden perspectieven geschetst voor onderzoek naar de lampstarter en de multilaag condensatortoepassingen. Voor de multilaag condensatoren lijkt emulsietechnologie een veelbelovende kandidaat omdat de gevormde deeltjes direct gebruikt kunnen worden bij tape casting. Daarnaast is ook onderzoek naar condensatoren zonder een aparte vormgevingsstap voor de elektrode en de keramische laag interessant. Voor toepassing in lamp starters lijken vooral de controle op de samenstelling en de poedermorfologie erg belangrijk. Ook moet nog worden onderzocht wat de belangrijkste oorzaak is van de verlaging van de maximum diëlektrische constante. Tenslotte is het noodzakelijk om een standaard methodevoor de analyse van de homogeniteit van keramische materialen te ontwikkelen.

Dankwoord

Mijn promotietijd is vooral een leerzame periode geweest. Uiteraard is het hier beschreven onderzoek niet het werk van een enkel persoon. De personen die mij de afgelopen vier jaar hebben geholpen wil ik hierbij bedanken:

Allereerst Henk Verweij voor de mogelijkheid tot promoveren en daarnaast voor het blijven herhalen van de zin, "het is wel oké alleen taaltechnisch moet het een en ander nog veranderd worden". Dat ik in dit stukje tekst geen bullets gebruik zal hem waarschijnlijk sterk verontrusten, maar niet verbazen. Louis voor de interessante discussies en natuurlijk voor het vele nakijkwerk. Toch denk ik dat in tegenstelling tot jouw mening, ik toch in ieder geval één keer in de afgelopen vier jaar tijd iets op jouw bureau moet hebben gedeponeerd wat de goede tekstvolgorde bezat.

Philips Aachen for their financial support. Special thanks to Oliver Steigelmann who taught me the special features of barium titanate preparation and XRF measurements and performed most of the dielectric measurements. Herr Bauser for XRF measurements, Kurt Albersten, Pim Groen and dr Hennings for fruitful discussions concerning barium titanate related problems. Pim also for a very enjoyable evening with green wine at the conference banquet in Aveiro.

Govert en Marcel voor jullie bijdrage, speciaal op het gebied van de homogene precipitatie. Govert ook voor zijn verrassende bijdrage aan mijn lab-demo.

Daarnaast natuurlijk mijn kamergenoten van het eerste uur (René, André, Zeger), van het tweede uur (Bas, Han en Maarten) en het laatste uur (Wim en Mercedes) voor jullie support en verdraagzaamheid. Vooral met Bas en Wim hebben we de 1733-gedachte, als een van de meest gezelligste werkplekken van de UT, gestalte kunnen geven, wat natuurlijk niet ten koste ging van de productiviteit (toch??).

Daarnaast het poederbroedergenootschap: Caroline, He, Bas, Tomas en Louis voor de goede samenwerking. De technici Claudia, Jose, Atilla en Nicole voor jullie bijdrage. Karin voor het eindeloos bestellen van chemicaliën, discussies over veiligheid, afwassen en het weer afvoeren van chemicaliën.

Maarten, Govert en Mark voor het aandachtig lezen van het gehele proefschrift. Mark ook om aan te geven dat de fabriek van het oxalaatproces voor bariumtitanaat vlakbij Haps ligt. N.B. De resterende taalfouten zijn voor mijn rekening.

Voor de goede werksfeer natuurlijk de bovenstaande personen maar vooral ook beide buurvrouwen, Baukje en Renate alsmede Arian, Eddy, Elise, Tomas, Matthijs, Fiona, Marjo, Cindy, Nieck en Natascha.

Voor metingen en andere bijdragen, Henk, Herman, Bernard (tevens voor zijn koekjes), Joop, Mark, Rico, Albert (UT) en Peter Karduck (TH Aachen).

Daarnaast de hele vakgroep en een ieder die ik vergeten ben, voor een erg leuke tijd in het uiterste oosten van het land.

Tenslotte wil ik in het bijzonder Angela heel erg bedanken voor haar steun en be-langstelling tijdens de afgelopen vier jaar.

Levensloop

Sven van der Gijp werd op 27 maart 1971 geboren te Amstelveen. In 1988 behaalde hij aan de Rijksscholengemeenschap te Schagen het HAVO diploma, waarna hij in datzelfde jaar aan de hogere laboratorium opleiding van de Hogeschool Alkmaar, toen nog gevestigd in Beverwijk, scheikunde ging studeren. Deze opleiding werd in juni 1992 afgesloten met een stage en een afstudeerperiode bij het Koninklijke Shell Laboratorium in Amsterdam. Tijdens de stage werd een literatuurstudie verricht naar het markeren van organische moleculen met kortlevende radiofarmaceutica voor positron emissie tomografie. Tijdens de afstudeerperiode werden actieve zepen gesynthetiseerd en gekarakteriseerd. Het HLO diploma werd behaald in juni 1992.

De verkorte studie scheikunde werd gevolgd van september 1992 tot mei 1994 aan de Universiteit van Amsterdam en werd in 1994 afgesloten met een hoofdvakstage onder begeleiding van prof. dr P.W.N.M. van Leeuwen met als onderwerp de synthese, karakterisering en het testen van de katalysatoreigenschappen van terugwinbare rhodium metaalcomplexen. Het doctoraal diploma werd in december 1994 behaald.

Van juni 1994 tot juni 1998 was hij werkzaam als assistent in opleiding bij de groep Anorganische Materiaalkunde van de Faculteit der Chemische Technologie van de Universiteit Twente. Het onderzoek werd uitgevoerd onder begeleiding van prof. dr ir H. Verweij en dr A.J.A. Winnubst. Een groot deel van het onderzoek dat gedaan is in deze periode is beschreven in dit proefschift.

Tijdens zijn promotietijd was hij voor enige tijd secretaris en voorzitter van het Twents AIO Beraad en daarnaast lid van het overleg wetenschappelijke directeuren (OWD) van de Universiteit Twente.

1. Introduction

Ferroelectric properties of pure and doped barium titanate

Barium titanate based ceramics are important for several electrical devices, such as multilayer ceramic capacitors, lamp starters and thermistors. Most of these applications are based on the ferroelectric behaviour of barium titanate, which was described first in literature in 1946 by Vul and Goldman [1,2].

The basic crystalline structure of $BaTiO_3$ above 130°C is the ideal cubic perovskite structure. Below this temperature (the so-called Curie-temperature) $BaTiO_3$ is tetragonal. When the temperature is decreased further, the structure of $BaTiO_3$ gradually changes from tetragonal to orthorhombic and finally to rhombohedral [3-5], see also *figure 1*. The latter two phases are ferroelectric as well.

In the cubic perovskite phase, the barium and oxygen ions together form a face-centered cubic lattice (fcc), with titanium ions positioned on octahedral interstices, see also *figure 1* [3]. Due to the large size of the barium ions, the size of the cell of the face-centered cubic BaO_3 (fcc) is enlarged so that the stability of titanium ions in the octahedral interstices is considerable less than in a comparable more close-packed configuration. Consequently, there are minimum-energy positions for the titanium ion, which are off centre and consequently give rise to an electric dipole [3-5]. This situation occurs when the material is in the tetragonal, orthorhombic or rhombohedral phase and results in a permanent dielectric dipole [3-5]. This is schematically shown in *figure 1*.

In the tetragonal unit cell two cell axes can be defined, one parallel to the Ti-O_1 axis (*a*) and the second one perpendicular to the Ba-O_2 axis (*c*). The change of the *a* and *c* axis with temperature and its influence on the dielectric behaviour is shown in *figure 2*.
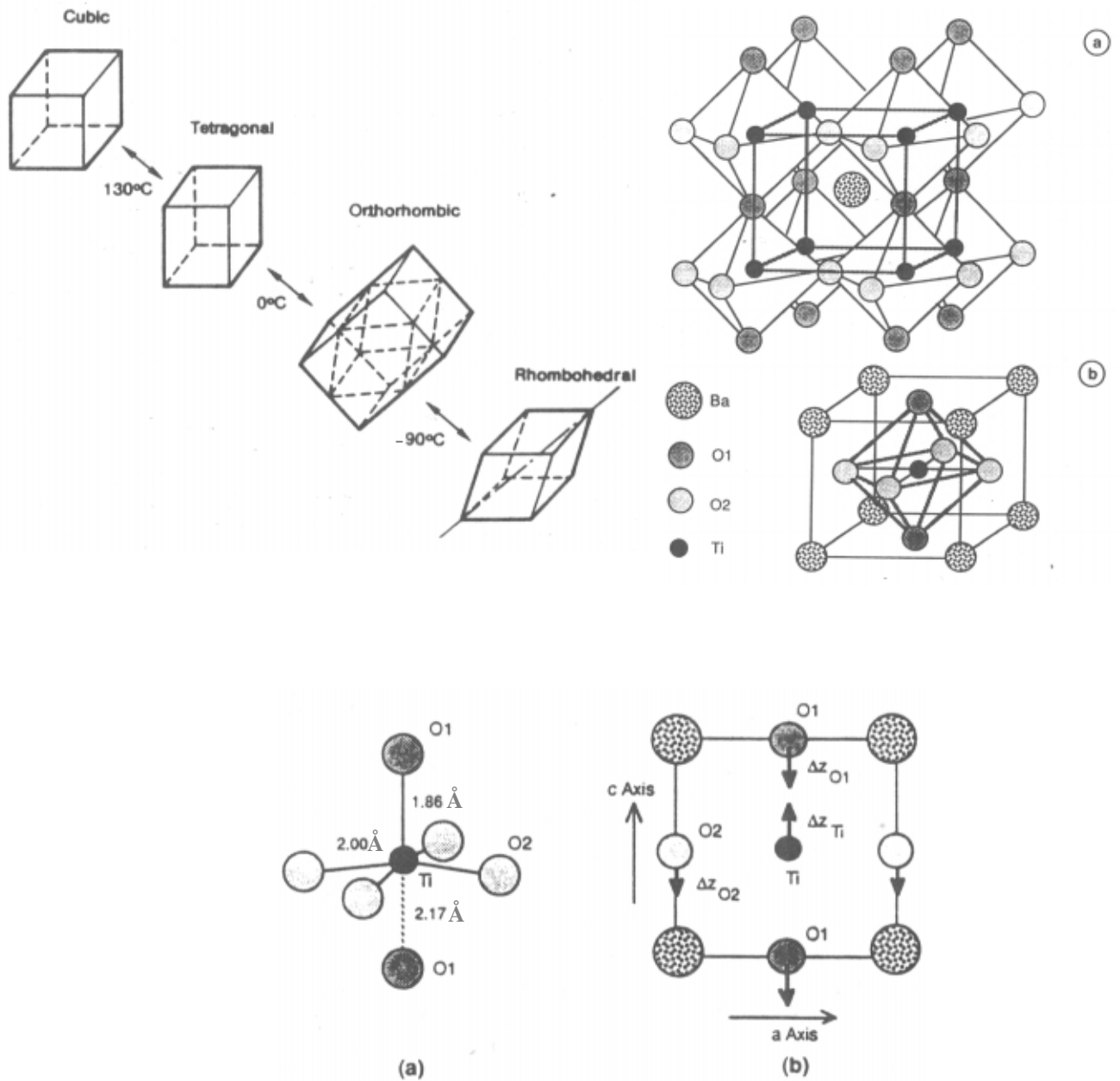
Figure 1: Top right: Phase transition of barium titanate, top left: cubic perovskite structure of barium titanate, (a) origin on titanium, (b) origin on barium ion [4]. Below: Ti-offset that creates permanent dipole, for explanation of the atoms see top left. (a) Distortion of the TiO_6 octahedron; (b) schematic projection on (010). The oxygen ion superimposed upon Ti is omitted [4].
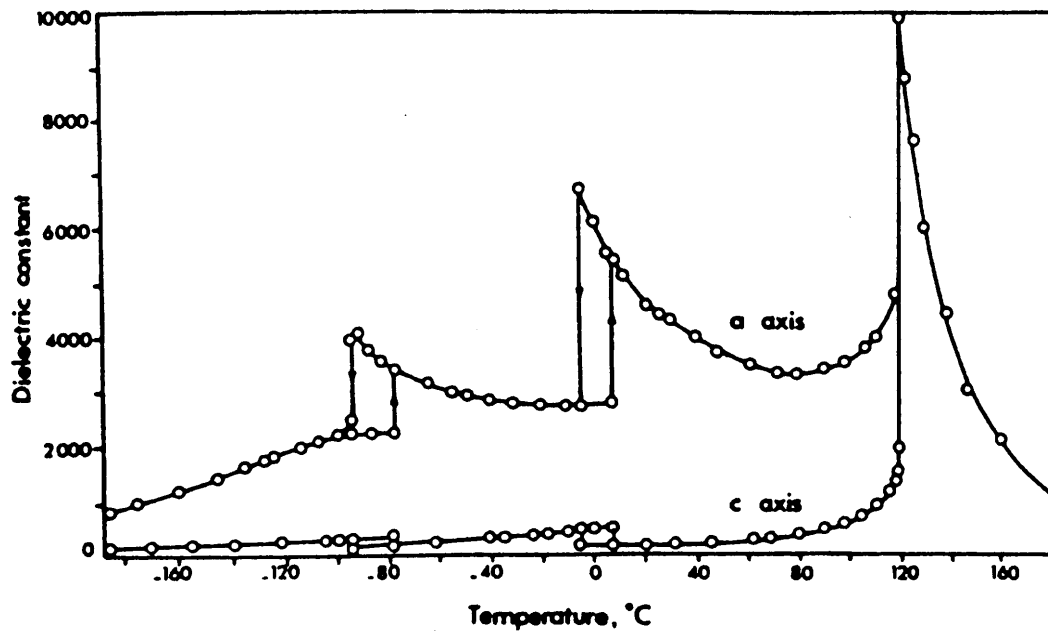
*Figure 2: Dielectric behaviour of undoped barium titanate with respect to the contri-
bution of the polarisation in the a and c direction.*

The low value of the dielectric constant ε for the cubic perovskite phase is a result of
the low polarisability of this phase. In case of the tetragonal phase a low polarisability
is present in the *c* direction, while the titanium ions are relatively free to vibrate in the *a*
direction. As a consequence both cell polarisability and dielectric constant are high in
the *a* direction.

The increase of the polarisabilty and therefore the increase in dielectric constant in the
vicinity of the phase transition temperatures is caused by a less stable lattice structure in
these regions. This results in a larger mobility of the Ti-ions inside the oxygen octahe-
dron and, consequently, in a larger polarisability and a higher relative permittivity[*].

1.1   Multilayer ceramic capacitor

A capacitor material is a material with a high relative permittivity, which can be used to
increase the capacitance of a capacitor. This is achieved by placing the capacitor mate-
rial between the electrodes. The capacitor material must satisfy certain demands. For

---

[*] Relative permittivity $\varepsilon_r = \varepsilon/\varepsilon_{vacuum.}$

instance the dielectric constant must be high but may also not depend too much on the temperature.

To create an effective capacitor, a number of disc capacitors are combined with a multilayer ceramic capacitor (MLCC), see *figure 3*. A MLCC with *n* effective layers is equivalent to *n* disc capacitors in parallel, of the same dielectric material (permittivity: ε), the same thickness *e* and the same effective area S [4, 6-9], see also *figure 3*. Therefore, a high capacity can be obtained in a relatively small volume. MLCC's are used for several applications and can be found in e.g. automobiles, PC's, TV's, VCR's and space shuttles [10].

For application in an MLCC the dielectric behaviour of barium titanate has to be adjusted. Instead of the small peak of the dielectric constant at 130°C, like in *figure 2*, the maximum of the dielectric constant must be around room temperature and its value should be less temperature-dependent. Both conditions can be achieved by the addition of dopants to the barium titanate.
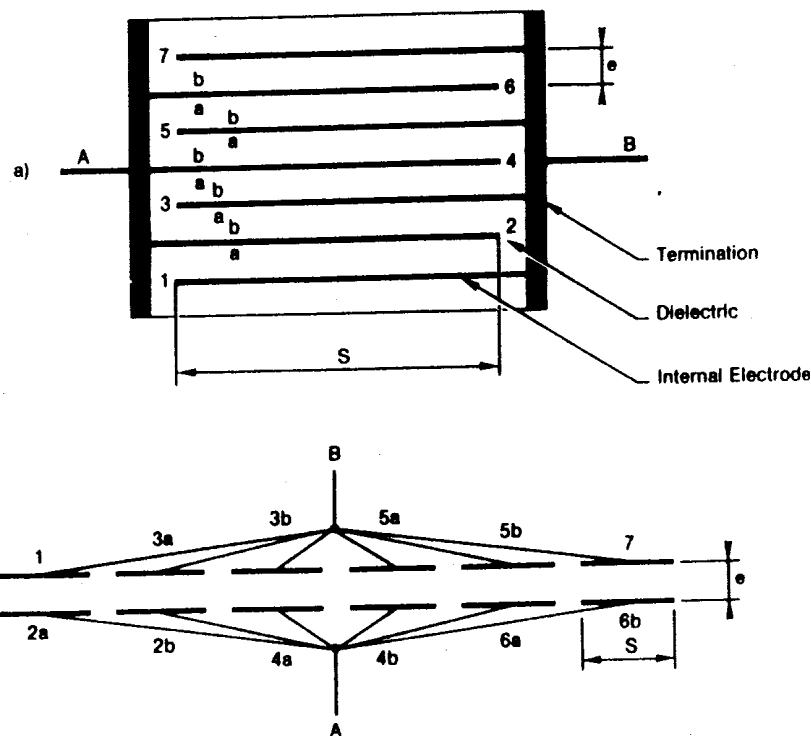

Figure 3:   Schematic overview of the basic principles of a multilayer ceramic capacitor [4].

4

The common method to prepare doped barium titanate is the mixed oxide method, which is based on the mixing and milling of metal oxides and carbonates. However, due to the on-going miniaturisation of electronic components in the last decades, new demands have to be met for the material properties of the MLCC and therefore for the production of these types of ceramics [6, 11-12]. A second important factor for the renewal of the production process of an MLCC is cost-reduction. A third important motive for changing the production of electroceramics is the increasing care for the environment. In case of the MLCC, capacitors that, amongst others, contain lead may result in better material properties [13-15]. However, since the use of lead in these devices has to be avoided for environmental reasons, barium titanate based systems are still preferred.

1.1.1 Material properties

To improve the performance of a MLCC per volume unit two options are possible:

- Raising of the dielectric constant of the dielectric layer
- Reduction of the dielectric layer thickness

The first option is not really an alternative any more. After 45 years of optimisation of $BaTiO_3$ ceramics the enhancement of the dielectric maximum has obviously come to a certain limit of approximately 16.000 in Y5V[*] materials [8]. Of course other materials other than barium titanate can be used but these alternatives are restricted by amongst others environmental demands.

The second option is the most promising. Thinner layers will results in more layers per unit volume. Naturally, the decrease in layer thickness has also consequences for the dielectric breakdown and electrical degradation under DC field stress [8]. To reduce the layer thickness powders have to be developed with smaller, better-defined particle sizes. The well-defined morphology also decreases the sintering temperature. This allows the use of less noble and consequently less expensive electrode materials.

A powder suitable for the production of thin layers of barium titanate should have a narrow aggregate size of 0.2-10 µm and a good sinterability. Also the introduction of dopants, such as calcium, zirconium and manganese should be possible. The ceramic must have a high relative dielectric constant (ε) and should be resistant to electrical

---

[*] Standard of the Electric Industries Association (EIA).

breakdown, and finally satisfy the Y5V specifications. Note that the height of ε depends on the required temperature specification of the capacitor.

In this thesis little attention is paid to the production of ceramics. However, the production of inorganic powders is studied. This powder preparation process must be compatible to normal industrial scaling-up requirements and the powders may have a cost price up to 12 Euro·kg^{-1}.

1.1.2 Composition

As mentioned before it is necessary to optimise the dielectric behaviour of BaTiO$_3$ dielectrics by adding dopants. Most of the dielectric mate-

Figure 4: Effect of doping on the phase transition temperature of barium titanate.

rials are based on mixed crystals of (Ba, Ca)(Ti, Zr)O$_3$. The doping with calcium and zirconium strongly inhibits the grain growth during sintering [3,8-10]. Since the dielectric behaviour of the mixed crystals is strongly related to the grain size, doping with calcium and zirconium results in a strong broadening and flattening of the dielectric maximum [8,9]. *Figure 4* shows the effect of several dopants on the phase transition temperatures.

Besides inhibiting grain growth, doping with zirconium also has an effect on the order of the phase transition at the Curie-temperature, which changes upon first to second order with increasing zirconium content, which has the consequence that Curie-temperature (T_c) and the Curie-Weiss (T_0) temperature coincide. According to the Curie-Weiss formula this implies a rise in the height of the dielectric maximum [8].
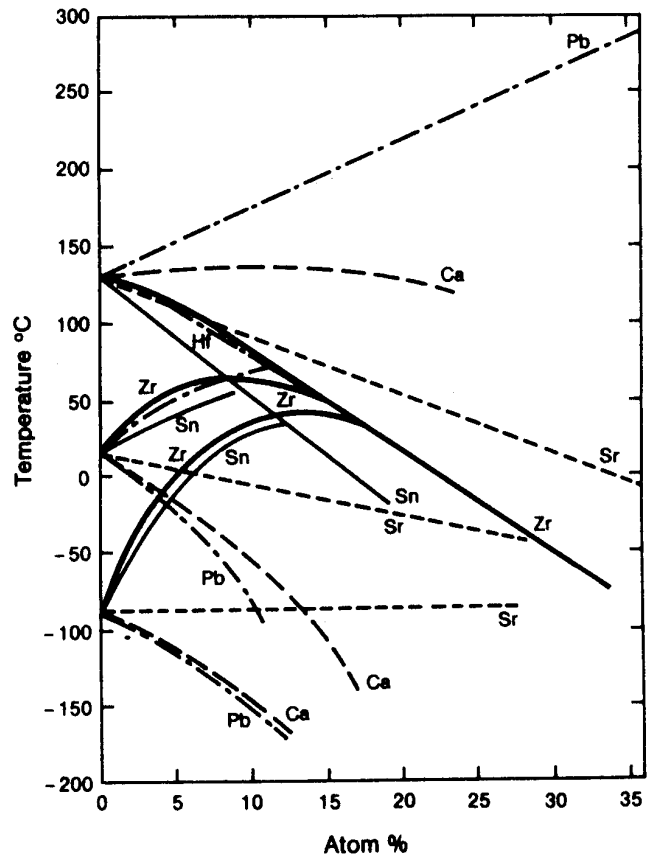
$\varepsilon_{r,max} = C_w/(T_c - T_o)$

In this equation C_w is the Curie constant. The Curie-Weiss temperature T_0 is determined by extrapolation $1/\varepsilon_r(T)$ to 0.

Other well-known dopants used for MLCC applications are amongst others: niobium, manganese and cerium [8,10, 16-17]. The latter element not only has effect on lowering and broadening of the ε versus temperature curve, but it has also a positive effect on the endurance of a MLCC [8].

1.1.3   Effect of the grain size on the dielectric constant

The reduction of the layer thickness has certain limits, for example the required strength of the ceramic layer as produced by tape casting. Another important aspect is the grain size dependence of the dielectric constant. The maximum value for the dielectric constant is obtained at a grain size of approximately 0.8 µm. The reason for this maximum in permittivity is not well understood. The most plausible explanation is based on the size of the ferroelectric domainstructure. When the grain size decreases, the size of the ferroelectric 90° domains will become smaller, and hence the material will have more but smaller domains. This indicates that the volume of domain walls increases with respect to the total domain volume. Since the permittivity of $BaTiO_3$ ceramics is considered to be the sum of a volume contribution and domain wall contribution, the increased permittivity of fine-grained $BaTiO_3$ can be explained primarily by a large number of 90° domains walls per unit volume. The large number of domain walls are a result of the small domain widths [18]. Other explanations for the height in maximum in permittivity are based on the amount of internal mechanical stress, which creates a high energy crystal lattice, which is likely to undergo a phase transition to the more favourable cubic phase [19-20].

This limit in permittivity restricts the minimum layer thickness of the dielectric ceramic layers. Reduction of the layer thickness is also limited by dielectric breakdown and electrical degradation under a DC field stress [8].

At the beginning of this project, the aim of research was focused on the multilayer ceramic capacitor. After two years, more attention was paid to the lamp starter application. However, some aspects of the first project play a role in the lamp starter project.

One of the major primary goals for the MLCC project was the development of an industrially feasible process for the preparation of the zirconium doped barium titanate powder, which implies that expensive starting materials, for example barium isopropoxide, had to be avoided, but also that the synthesis had to be performed in the absence of extreme conditions, like e.g. high pressure or nitrogen atmosphere. These boundary conditions had effect on the choice of the preparation route. The selected preparation method was developed further for the application as lamp starter, where cost-price conditions were less strict.

1.2   Application in lamp starter

Barium titanate-based ceramic materials can be used as well in a contact less starting device [17], which can be applied in a fluorescent lamp, a mercury lamp and a discharge tube, such as a sodium vapour lamp. The working principle of the lamp-starter is described in appendix 1.

In non-linear elements the electric charge is constant when the electric field is below a value $-E_0$ or above a value E_0. When an alternating current is applied, the abrupt change of the charging current takes place at the value $(\pm)E_0$. This abrupt change only occurs in barium titanate ceramics with an exceptionally high dielectric maximum at the Curie-temperature [21]. This high value for the dielectric constant can only be obtained when the three phase transitions in barium titanate coincide, which occurs when barium titanate is doped with approximately 10% zirconium.

The application of the pulse-generating device is based on the hysteresis properties, which are both closely related to the dielectric properties of the material. Below the Curie-temperature the hysteresis curve has the requires cubic-like shape. Therefore, the temperature at which the pulse generating devices can be used, lay well below the Curie point of the material rather than around the Curie-temperature as in the case for the MLCC.

1.2.1   Material properties

The first contact-less starting devices were based on single crystals [21]. Single crystals, however, are too expensive for ceramic application. Therefore, polycrystalline materials were developed with similar material properties. These polycrystalline materials are based on powders prepared by the mixed oxide method. Unfortunately, the de-

gree of mixing in mixed oxide powders compared to powders prepared by wet-chemical techniques is quite small. Since the rate of diffusion of ZrO_2 is rather slow [22], this difference in homogeneity may also result in a lower chemical homogeneity of the final ceramic. This chemical homogeneity has an influence on the dielectric behaviour of the ceramic[24, 25-27]. Therefore when the relation between dielectric constant and homogeneity is considered, ceramics prepared from a more homogeneous powder may result in a ceramic with better dielectric properties.

The homogeneity of a powder can be increased by using a wet-chemical preparation method or in other words: when a powder preparation process step is present in which the various metal species are in solution. Then the (almost) atomic mixing within the solution can be converted in the same extent of mixing in a solid product. This result in a higher homogeneity of this solid product and corresponding powder compared to the homogeneity of a mixed oxide prepared powder.

In conclusion, to obtain an extreme high value for the dielectric constant at the Curie-point temperature, three aspects are important:

- The phase transitions present in barium titanate, cubic-tetragonal, tetragonal-orthorhombic and orthorhombic-rhombohedric must overlap. This overlap of the three phase transitions can be obtained by the doping the barium titanate with zirconium [23-25]. The overlap of the phase transitions results in a Curie temperature of approximately 90°C. Consequently below the 90°C the material is ferroelectric and has the required type of hysteresis curve.

- For an optimal effect of the doping with zirconium it is necessary that the composition is the same throughout the entire ceramic. In other words, the ceramic must be chemically homogeneous. Deviations from the average composition will lead to different phase transition temperatures and therefore to a lower value of the maximum dielectric constant [22, 26].

- Since mechanical stress in the material gives rise to a decrease of the maximum value for the dielectric constant [27], the amount of stress in the ceramic must be as low as possible. The mechanical stress in the material is introduced in the material during cooling after sintering. At the Curie-temperature the unit cell of the zirconium-doped barium titanate changes from cubic to rhombohedric, which creates mechanical stress. The amount of stress can be reduced when domains are formed.

Compared to small-grain ceramics, in relation to the amount of material, more domains are formed in large grain ceramics. 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. Consequently to promote grain growth, high sintering temperatures and liquid-phase sintering are required [29, 30].

1.3   Scope of this thesis

There is a vast amount of literature present on the wet-chemical preparation of barium titanate. However, in a great deal of these articles no attention is paid to the stoichiometry of the calcined powders neither to the sinterability of these powders. In chapter 2 an overview is given of preparation methods for barium titanate or related materials. The choice of preparation method is based on the required material properties described in this chapter, the desired method must be above all an inexpensive wet-chemical preparation method. The peroxo process is a promising preparation method for the preparation of doped barium titanate [30-32].

To optimise the powder and material properties the peroxo method has to be adjusted for the preparation of doped rather than undoped barium titanate. The preparation method must preferably satisfy demands described for the production of a MLCC. Chapter 3 describes the combination of the peroxo process with the oxalate process [34]. The latter is a commercial process based only used for the preparation of undoped barium titanate. The resulting so-called peroxo-oxalate process consists of a complexation-precipitation reaction of Ba, Ti and Zr with hydrogen peroxide and oxalate in alkaline environment. In order to gain insight in the formation of a homogeneous precipitate and subsequently calcined powder, the reactions that occur during this process and the nature of the precipitating complex are described in chapter 3.

Next to a high chemical homogeneity, the final calcined powder must be sinterable. In addition to the wet-chemical preparation process no alternations in the concentration ratio of the various elements may occur. In chapter 4 the influence of several reaction parameters on the phase purity and morphology of the calcined powders are described.

To obtain a sinterable powder, morphology control is important. Therefore, a number of preparation methods are tested which results in powders with an optimal morphology. These preparation methods are based on the peroxo-oxalate method. However, in-

stead of adding two solutions together to start precipitation, now all the elements are present in one system. To prevent direct complexation and precipitation one of the elements is masked, but is released by an increase in temperature. Three different precipitation mechanisms are studied in order to find the best preparation method with respect to morphology and stoichiometry.

In literature not much data on the determination and analysation of the chemical homogeneity is available. In this thesis several possible techniques are used and discussed. With these studies the chemical homogeneity of the wet-chemical prepared powders is compared to the homogeneity of a mixed oxide powder and a commercial wet-chemical (hydrothermal) powder. Most perovskites are completely miscible and any kind of thermal treatment gives rise to interdiffusion and improved distribution of the constituents. The distribution of extra elements like Zr normally takes place in $BaTiO_3$ materials during sintering and grain growth [33]. Due to the high sintering temperature and the long sintering time, both necessary to obtain large grains, it might be that, in spite of the slow diffusion rate of zirconium [22], diffusion rules out a lot of the differences in homogeneity created by the use of powders with different degrees of homogeneity [34].

Kazaoui and Ravez claim that a difference in the chemical homogeneity between a sol-gel prepared powder and a mixed oxide prepared powder is the reason for the lower dielectric maximum of the mixed oxide prepared ceramic [22]. However, no data is provided concerning the chemical homogeneity by these authors. However, Hennings et al. claim on the basis of evaluating X-ray diffraction line profiles in paraelectric and ferroelectric states, that internal stress and not chemical homogeneity seems to be the major reason for the local distribution of Curie-points in these materials [28]. In chapter 7 attention is paid whether or not the chemical homogeneity has effect on the dielectric properties also. The relation between the microstructure and the dielectric properties is discussed.

Finally, in chapter 8 suggestions for further research are given concerning MLCC's and lamp starters.

References

1. B.M. Vul and I.M. Goldman, "Dielectric constants of titanates of the metals of the second group," *Compt. Rend. Acad. Sci.URSS* **46** 139-42 (1945).
2. B.M. Vul and I.M. Goldman, "Dielectric constant of barium titanate as a function of strength of an alternating field," *Compt. Rend. Acad. Sci. URSS* **49** 177-80 (1945).
3. W.D. Kingery, H.K. Bowen and D.R. Uhlman, "Introduction to ceramics," 2nd ed. pp. 964-72 New York (1976).
4. A. Morell and J.-C. Niepce, "BaTiO$_3$-based materials for M.L.C. capacitors applications," *J. Mater. Educ.* **13** 173-232 (1991).
5. D.W. Richerson, "Modern ceramic Engineering," 2nd ed. pp. 263-66 New York (1992).
6. A. Okamoto, "Miniturization and integration of passive components by multilayer ceramic technology," pp. 1035-44 in *Electroceramics 4*, Aachen, Germany (1994).
7. Y. Yamashita, "PZN-Based relaxors for MLCCs," *Am. Ceram. Soc. Bull.*, **73** [8] 74-80 (1994).
8. D.F.K. Hennings, B. Schreinemacher and H. Schreinemacher, "High-permittivity dielectric ceramics with high endurance," *J. Eur. Ceram. Soc.*, **13**, 81-88 (1994).
9. L.E. Cross, "Relaxor ferroelectrics," *Ferroelectrics*, **76** 241-67 (1987).
10. M.S.H. Chu and A.W.I.M. Rae, "Manufactoring dielectric powders," *Am. Ceram. Soc. Bull.*, **74** [6] 69-72 (1995).
11. L. Sheppard, "Progress continues in capacitor technology," *Am. Ceram. Soc. Bull.*, **72** [3] 44-56 (1993).
12. D. Hennings, M. Klee and R. Waser, "Advanced dielectrics: bulk ceramics and thin films," *Adv. Mater.* **3** [7,8] 334-340 (1991).
13. A. Nijmeijer, H. Kruidhof and D. Hennings, "Synthesis and properties of lead magnesium niobate zirconate relaxor materials," *J. Am. Ceram. Soc.*, **80** [10] 2717-21 (1997).
14. C.G.F. Stenger, "Diffuse phase transitions and ordening in some ferroelectric perovskite," Thesis, University of Twente (1980).
15. K. Keizer, "Ferroelectric properties, non-stoichiometry and microstructure of substituted lead titanate ceramics," Thesis, University of Twente, (1976).
16. M. Gilbert and P.-H. Duvigneaud, "Effect of Mn on microstructure and electrical properties of Nd-doped BaTiO$_3$," pp. 1919-23 in *Euro-Ceramics II*, Proc. 2nd Int. Conf. on electroceramics and ceramics for special applications (Augsburg, September, FRG, 1991). Edited by G. Ziegler and H. Hausner. Deutsche Keramische Gesellschaft, (1991).
17. M. Kahn, "Influence of grain growth on dielectric properties of Nb-doped BaTiO$_3$," *J. Am. Ceram. Soc.*, **54** [9] 455-57 (1971).
18. D. Hennings, "Grain size and grain boundary effects in passive electronic components," *Surface and Near-surface chemistry of oxide materials*, Ed. by J. Nowtny and L.-C. Dufour, Amsterdam, 479-505.
19. D. Hennings, "Diffuse ferroelectric phase transitions in Ba(Ti$_{1-y}$Zr$_y$)O$_3$ ceramics, " *J. Am. Ceram. Soc.*, **65** 539-44 (1982).
20. N. Bernaben, A. Leriche, B. Thierry , J.C. Niepce and R. Waser, "Pure barium titanate ceramics: crystalline structure and dielectric properties as function of grain size," pp. 105-09 in *Electroceramics 4*, Aachen, Germany (1994).
21. S. Iwaya, H. Masumura, Y. Midori, Y. Oikawa and H. Abe, United States Patent, 4,404,029, "Non-linear polycrystalline barium titanate dielectric element".
22. S. Kazaoui and J. Ravez, "Dielectric relaxation in Ba(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ ceramics prepared from sol-gel and solid state reaction powders," *J. Mater. Sci.*, **28** 1211-19 (1993).
23. S.M. Neirman, "The Curie point temperature of Ba(Ti$_{1-x}$Zr$_x$)O$_3$," *J. Mater. Sci.*, **23** 3973-80 (1988).

24. R. McSweeney, K. Zuk and D. Williamson, "Square loop Ba(Ti,Zr)O$_3$ capacitors based on alkoxide derived (Ti,Zr)O$_2$ powders," First international conference on ceramic powder processing science, Orlando, Florida.

25. B. Jaffe, W.R. Cook Jr and H. Jaffe, "Piezoelectric ceramics," Academic press, New York 53-114 (1973).

26. P.P. Phule and S.H, Risbud, "Review, Low-temperature synthesis and processing of electronic materials in the BaO-TiO$_2$ system," *J. Mater. Sci.*, **25** 1169-83 (1990).

27. D. Hennings, "Barium titanate based ceramic materials for dielectric use," *Int. J. High Tech. Ceram.*, **3** 91-111 (1987).

28. D.F.K. Hennings, R. Jansen and P.J.L. Reynen, "Control of liquid-phase-enhanced discontinuous grain growth in barium titanate," *J. Am. Ceram. Soc.* **70** [1] 23-27 (1987).

29. A. Recnik and D. Kolar, "Exaggerated growth of hexagonal barium titanate under reducing sintering conditions," *J. Am. Ceram. Soc.*, **79** [4] 1015-18 (1996).

30. G. Pfaff, "Herstellung von BaTiO$_3$ Pulver durch Fallung von BaTiO$_2$(O$_2$)·3H$_2$O," *Z. Chem.* **28** [2] 76-77 (1988)

31. G. Pfaff, "Synthesis and characterization of BaTi$_2$O$_5$," *J. Mater. Sci. Lett.* **9** 1145-47 (1990)

32. G. Pfaff, "Sol-gel synthesis of barium titanate powders of various compositions," *J. Mater. Chem.* **2** [6] 591-594 (1992).

33. W.S. Clabaugh, E.M. Swiggard and R. Gilchrist, "Preparation of barium titanyl oxalate tetrahydrate for conversion to barium titanate of high purity," *J. Nat. Bur. Stand.*, **56** [5] 289-291 (1956).

34. D. Hennings and G. Rosenstein, "Temperature-Stable dielectrics based on chemically inhomogeneous BaTiO$_3$," *J. Am. Ceram. Soc.*, **67** [4] 249-54 (1984).

Appendix 1

Operating principle pulse generating device

The operating principle of the pulse generation is schematically drawn in *figure 5* [21]. The voltage pulse (V_p), necessary to start the electrical devices, arises when an alternating current (V_{ac}) is applied and is the result of an abrupt change of the charging current (I_c). Due to this change, the material will respond by generating a high voltage peak as a consequence of Faraday's law. The abrupt change in charging current is due to field-induced simultaneous flipping of the titanium position in barium titanate or in other words by an abrupt change in the slope of the non-linear polarisation (D) versus
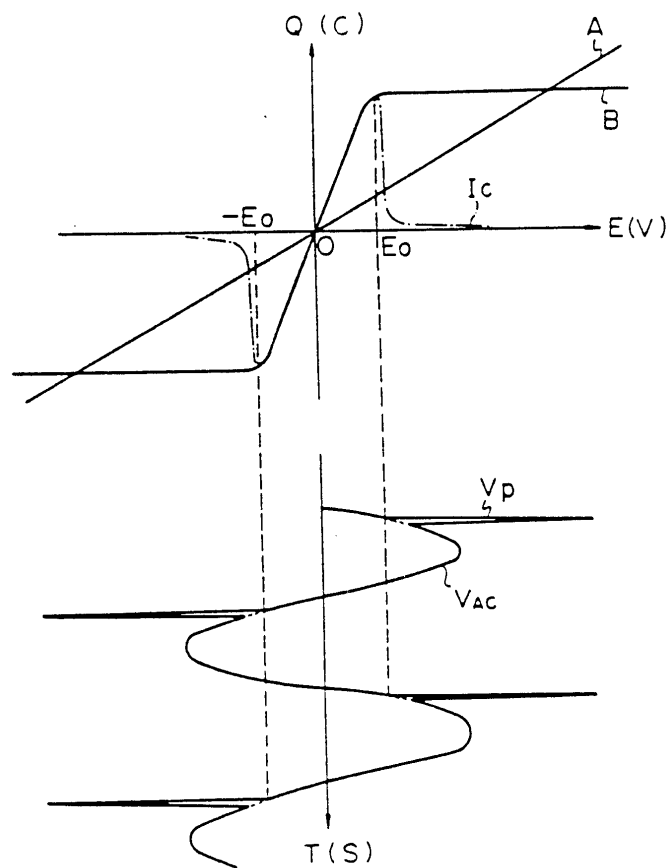

Figure 5:   Schematic overview of the basic principles of a pulse-generating device [21].

electric field (E) hysteresis loop. In this way, two pulses, one positive and one negative are generated in a full oscillation cycle. The abrupt change in charging current only takes place in non-linear materials, represented by situation B in *figure 5*. When an alternating current is applied in linear materials (situation A) no saturation occurs, consequently there is no abrupt change in the charging current and hence no voltage peaks are obtained.

2. Overview on the synthesis of (doped) barium titanate

2.1 Introduction

The large number of applications based on barium titanate related materials has given rise to many publications concerning the preparation of this material. Most of these papers, however, only describe the powder preparation method and do not give any details on further stages of the process such as sinterability, microstructure and composition after processing.

In this chapter an attempt is made to give a systematic survey of the possible preparation methods for barium titanate. Part of these preparation methods have been used as starting points for the work, described elsewhere in this thesis.

The preparation of barium titanate is mainly performed in two ways:

- Mixed oxide (or solid state) preparation.

- Classical wet-chemical preparation methods, so called because of the use of a solvent. The latter methods are sometimes referred to as sol-gel methods. Note that this term is not correct because in the majority of the wet-chemical processes described in literature neither a sol, nor a gel is formed.

In this chapter attention is paid to the preparation of barium titanate powders in which the introduction of dopants like zirconium and calcium is possible. For both lamp starter and MLCC applications a sinteractive powder is required. Consequently a small particle size and a low degree of aggregation are a requirement for the calcined powders. Chemical homogeneity and control of the final composition of the powder are important too.

In this review only classical wet-chemical preparation techniques are discussed. No attention is paid to a possible combination of the preparation methods with homogeneous precipitation or emulsion technology. Also no attention is paid to vapour deposition techniques, such as e.g. electrochemical vapour deposition. It is believed that these techniques are not suitable for large-scale preparation of bulk ceramics.

2.2   Mixed oxide preparation

Mixed oxide processes for the preparation of doped barium titanate are based on $BaCO_3$ and TiO_2 powders as starting materials. If necessary, dopants like ZrO_2 can be introduced. The process starts with the mixing and milling of the precursors, after which calcination takes place. During calcination barium titanate is formed. After calcination mixing and milling is repeated [1-7].

The solid state method is often used because of the relatively low number of processing steps and the low process costs. The powders obtained with this method, however, suffer from a number of disadvantages [6]:

- Due to the high calcination temperature, the calcined powders consist of large aggregated particles that are shaped irregularly.
- Due to the degree of mixing, the homogeneity of the powder is sometimes insufficient. As was determined with high temperature XRD, some barium carbonate phase may remain even after calcination at temperatures as high as 1100°C.
- Impurities in the powders can be introduced as a consequence of the various milling steps needed.
- A slight deviation from the desired composition may arise due to evaporation as a result of the high calcination temperature necessary to obtain one single phase material.

The poor morphology of the mixed oxide powders results in a low sinterability and consequently, high sintering temperatures are necessary, which results in a ceramic with a high relative porosity [7]. For these reasons, improvements in the material properties might be possible when the ceramics are made from a wet-chemically prepared powder at the expense of a higher cost price and a more complicated process.

To compare the mixed oxide preparation method with wet-chemical preparation techniques it is necessary to study the morphology and the densification behaviour of the mixed oxide powder. A barium titanate powder, prepared according to the mixed oxide method and calcined at 1100°C, shows a typical average particle size of around 1 µm. The average size was reduced by milling to 0.4 µm. A compact prepared from the mixed oxide powder started to densify at approximately 1100°C and had a

maximum densification rate at 1277°C. The densification was finished at 1360°C, after which a density of 97% is obtained.

2.3 Wet chemical processes

The wet-chemical powder preparation methods described in this chapter are distinguished from each other according to the physical-chemical concept on which they are based. With a few exceptions all these processes have in common that an intermediate is formed during the preparation process, starting from a precursor solution. In the intermediate the chemical composition is fixed (or immobilised) either chemically or physically in such a way that during the next processing step the chemical composition will not change. The final powder is normally obtained by calcination of the intermediate during which polycrystalline barium titanate is formed. The various wet-chemical techniques differ in the formation mechanism of the reaction intermediate. Chemical immobilisation methods can be subdivided further into complexation or gelation methods whereas physical immobilisation methods can be subdivided into precipitation and dispersion methods. A combination of complexation and precipitation is possible as well. When compared to powders prepared with the mixed oxide method, wet-chemical preparation methods generally have the following advantages:

- Fine particles with a high sinterability.
- Improved chemical homogeneity.
- Less contamination because milling can be avoided.

However, wet-chemical preparation methods might have the following disadvantages:

- More and complicated processing steps.
- Due to differences in solubility between various ions, the use of wet-chemical preparation methods can result in deviations from the desired stoichiometry.
- The use of solvents is often not incompatible with health and environmental regulations, the same goes for thermal decomposition of organic reagents.
- The small particles which are formed in the solution, are very reactive so that special precautions must be taken in order to prevent aggregate formation.

- Finally, a low concentration is required and hence a low yield is obtained. The yield can, however, be increased by using continuous preparation as described for example by Kuntz [8] and Ocaña [9].

In the next sections attention is paid to the morphology, sinterability and the stoichiometry of the powder produced with the several methods.

2.4   Complexation techniques

Complexation reactions are based on the formation of a polymer network, in which the metal ions are distributed homogeneously, but they are not present in the backbone of this polymer network.

Complexation methods start by dissolving the various metal ions, followed by the addition of complexing agents, see also *figure 1*. Next, either a pyrolysis, precipitation or dispersion process is used to convert the metal ions in solution into a solid product.
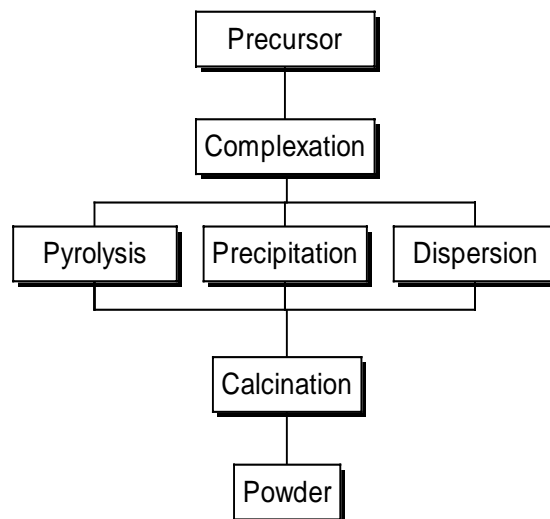
```
              ┌─────────────┐
              │  Precursor  │
              └──────┬──────┘
              ┌──────┴──────┐
              │ Complexation│
              └──────┬──────┘
     ┌───────────────┼───────────────┐
┌────┴─────┐  ┌──────┴──────┐  ┌──────┴─────┐
│ Pyrolysis│  │Precipitation│  │ Dispersion │
└────┬─────┘  └──────┬──────┘  └──────┬─────┘
     └───────────────┼───────────────┘
              ┌──────┴──────┐
              │ Calcination │
              └──────┬──────┘
              ┌──────┴──────┐
              │   Powder    │
              └─────────────┘
```

Figure 1: Processing steps in the complexation method.

2.4.1   Pyrolysis

Complexation in combination with pyrolysis results in the direct conversion of the precursor solution, containing the metal ions, to a powder. Hence, no washing step is possible. The lack of the washing step makes it necessary to start the process with counter ions that can be removed by means of thermal decomposition. Therefore, nitrate- or carbonate-salts are suitable as precursor, whereas sulfonates and chlorides are not.

Another drawback of the complexation method is the fact that during pyrolysis local so-called "hot-spots" can be formed. These hot spots are caused by the presence of inflammable organic residues and lead to aggregate formation [10]. The high weight losses and the formation of environmental-unfriendly gasses may restrict the use of the pyrolysis methods too.

By using the apparatus described by Kuntz it is possible to operate the pyrolyses process in a continuous mode. In that case, the solution containing the metal ions and complexating agents is led through the flame of a gas burner, in which pyrolysis occurs instantaneously [11].

2.4.1.1 Pechini process

The Pechini or mixed-liquid process starts by mixing the desired metal cations in an aqueous solution [8,12]. To this solution chelating agents are added such as e.g. ethylene glycol and citric acid (α-hydroxycarboxylic acid). The use of other complexing agents is described in literature too [13]. The metal ions form a complex with the citric acid. The next step in the Pechini process is heating to a temperature around 110°C, where esterification between the carboxylic groups from the citric acid molecules and the hydroxy groups from ethylene glycol takes place. The esterification results in the formation of a resin, according to the mechanism depicted in *figure 2*. The resin is either pyrolysed followed by calcination [8, 14] or calcined directly, in which case the pyrolysis step takes place during calcination [7,8]. This method has first been
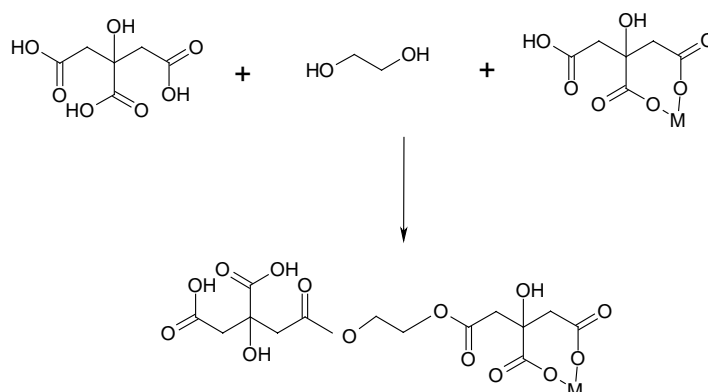

Figure 2:   *First stage of the formation of a network in the Pechini Process. M = metal ion.*

described by Pechini for the preparation of barium titanate [4], but other examples are known with elements like zirconium, calcium and manganese in combination with various counter ions such as chlorides, hydroxydes, isopropoxides and nitrates [14,15]. It is also possible to perform the Pechini process in non-aqueous environment. Finally, the Pechini method has been described for the preparation of thin layers for use in electrical capacitors as well [7,15].

The average aggregate size of powders prepared by the Pechini method is approximately 150 nm, but these aggregates are associated into larger agglomerates. Densification of a barium titanate green body starts at 900°C and is completed at 1300°C, which results in a ceramic with a density of 99%. The maximum densification rate is around 1100°C [16].

2.4.1.2 Citrate synthesis

The citric acid method starts with the addition of nitrate salts to an aqueous solution of diluted citric acid, after which the solution is neutralised by addition of ammonia. The metal ions are complexed by citrate ions. Due to the presence of large amounts of organic molecules and the presence of ammonium nitrate spontaneous combustion occurs when the solution is heated. The resulting solid product is calcined to remove residual organic fragments and to form polycrystalline barium titanate. The citrate synthesis is described for the preparation of barium titanate by Hennings et al. [16].

A powder prepared according to the citrate synthesis has an average grain size around 2 µm. During sintering at 1400°C the density increased from 66% to 99% [17].[1]

Compared to the resin formed with the Pechini method, the resin formed with the citrate method is less viscous, so that the citrate method is somewhat less effective in immobilisation. On the other hand, far less organic material has to be used, which results in fewer hot-spots and consequently, a less aggregated powder.

2.4.1.3 EDTA synthesis

The EDTA synthesis is closely related to the citric acid method, but instead of citric acid EDTA is used as complexing agent. The process has been described in literature with either pyrolysis [18, 19] or direct calcination [19,20]. In the latter method

---

[1] Note that the green structure of a compact strongly depends on the processing conditions, which in turn has an influence on the sintering properties.

(*figure 3,* route II), described for the preparation of barium titanate, the metal ions are added first to an aqueous solution of EDTA. During addition the pH is kept constant at 5 by adding an aqueous ammonium hydroxide solution, after which the solvent is evaporated in a vacuum oven. This results in the formation of a viscous liquid, which is subsequently calcined [20].

A representative SEM-micrograph of the morphology of a calcined powder obtained with the EDTA method is given in *figure 4*. The powder morphology consists of soft flakelike agglomerates, built up of dense aggregates of approximately 2 µm. After calcination a small barium excess is found with XRF. This excess might be caused by condensation of the titanium precursors, and results in a precipitate that sticks to the reactor vessel. No literature data are available on the sinterability of EDTA-prepared barium titanate powders. The use of chloride precursors is not recommended because their presence will lead to differences from the desired phase composition in the calcined powder [20].
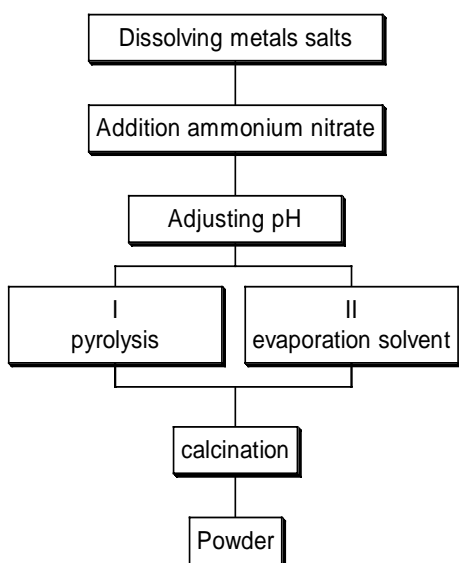
*Figure 3:   Flow scheme of the EDTA
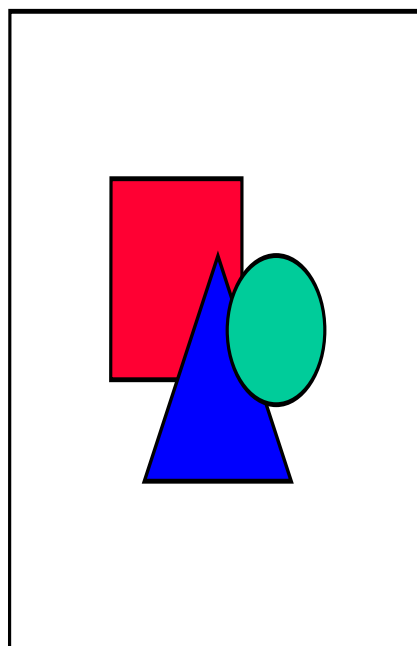   method.*

*Figure 4:   SEM-micrograph of
              calcined powder,
              prepared with the
              EDTA method.*

2.4.1.4 Stearic acid synthesis

The stearic acid method is not really a complexation technique, since no complexation occurs at all. The method is described by Wang et al. and starts by dissolving barium and titanium alkoxides in molten stearic acid [21]. After cooling a homogeneous resin is obtained. Calcination at 700°C results in a cubic perovskite barium titanate powder with a small titanium excess. The powder has an average agglomerate size of 10 µm, but consist of smaller particles with a size of approximately 0.2 µm. The specific surface area as measured with BET is 15 $m^2 \cdot g^{-1}$. The sinteractivity of a barium titanate powder prepared according to the stearic acid method has not been described yet.

2.4.2 Precipitation

2.4.2.1 The oxalate process

The oxalate process results in the formation of fine, stoichiometric powders and is one of the best processes for obtaining a barium titanate powder with a well-controlled stoichiometry [10]. The oxalate method starts with inexpensive inorganic compounds like titaniumoxychloride ($TiOCl_2$) and is performed in an aqueous environment. The oxalate method is commercially applied for the production of pure, undoped-barium
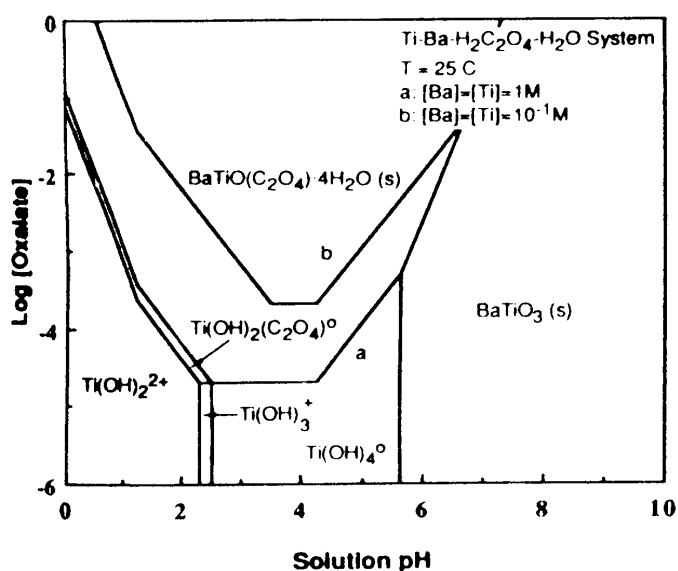
Figure 5: log [oxalate]-pH diagram for the Ti-Ba-$H_2C_2O_4$-H_2O system at 25°C with different metal concentrations; (a) [Ba] = [Ti] =
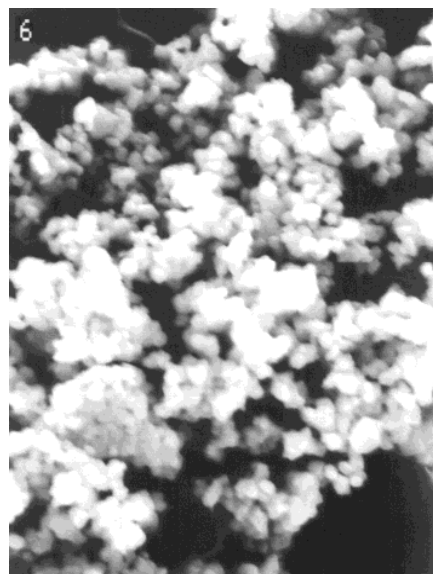
Figure 6: SEM micrograph of calcined powder prepared with the oxalate method.

titanate.[*] The oxalate process is based on the precipitation of a barium titanate oxalate complex in an acidic environment as is schematically shown in *figure 5*.

The process starts by dissolving the various metal salts in water. The titanium precursor, either $TiCl_4$ or $TiOCl_2$, is hydrolysed, followed by the addition of a barium salt. Next, at approximately 60-90°C the metal solution is added slowly to a saturated oxalic acid solution, which results in the formation of a precipitate [7,22-23].

$$Ba^{2+} + TiO(OH)_2 + 2C_2O_4^{2-} + 2H_3O^+ \xrightarrow{pH4,60°C} BaTiO(C_2O_4)_2 \cdot 4H_2O$$
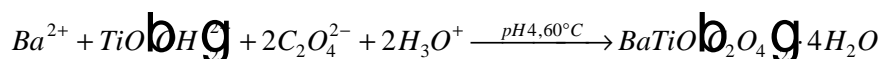
Important process parameters are the precipitation temperature, precipitation time and the ratio Ba/Ti [22]. With a careful choice of parameters it is possible to obtain a powder with a barium over titanium ratio of 1.000. The introduction of dopants with the oxalate method is not possible, since the replacement of barium by e.g. strontium or calcium is not easy, because these ions cannot precipitate stoichiometrically at a pH of about 4 [24], see also chapter 4.

The powders obtained with the oxalate method have a large average particle size due to the high precipitation temperature and slow titration rate, see also *figure 6* [22]. An improvement over the conventional oxalate method in water can be made when the precipitation process is conducted in an alcoholic solution with a higher titration rate [22]. The oxalate dissolves very well in ethanol, whereas titanium and barium ions do not dissolve at all. In this variation of the conventional oxalate process, a somewhat higher density of 98.5% is obtained after sintering. Note that after calcination second phases such as Ba_2TiO_4 or $BaTi_5O_{11}$ are often found [22]. These second phases are formed due to local differences in stoichiometry. During sintering, second phases may disappear when the sintering temperatures are sufficiently high.

2.4.2.2 Peroxide method

In the peroxide process the titanium and barium ions are combined with a hydrogen peroxide solution with a high pH to form an insoluble complex salt. The method starts with metal ions, like chlorides, nitrates, sulphates, etc., which are soluble in water. Ammonia or aqueous solutions of sodium hydroxide or potassium hydroxide can be used to increase the pH.

- TAM Ceramics, inc: Niagara Falls, N.Y. USA; Philips Uden, the Netherlands (near Haps).

The peroxide method starts by dissolving the various metal ions in an aqueous solution, see also *figure 7*. Then a hydrogen peroxide solution of equal volume as the precursor solution is prepared by mixing an ammonium hydroxide solution with an aqueous solution of hydrogen peroxide and water. The precursor solution is added slowly at 10°C under an argon atmosphere to the hydrogen peroxide solution [26-29]. A yellow precipitate remains, which is filtered off, washed, dehydrated with ethylacetate and finally dried with H_2SO_4. This results in the formation of the complex salt $BaTiO_2 \cdot (O_2) \cdot 3H_2O$. Subsequently the precipitate is heated to decomposition. Calcination below 600°C results in the formation of amorphous barium titanate, free of impurities and with a uniform and fine

```
┌─────────────────────────┐
│   Dissolving Metal salts │
│   Hydrogen peroxide      │
│   aqueous solution       │
└─────────────────────────┘
            │
┌─────────────────────────┐
│      Addition to         │
│ ammonium hydroxide solution │
│        pH = 9            │
└─────────────────────────┘
            │
      ┌──────────┐
      │ Washing  │
      └──────────┘
            │
      ┌──────────┐
      │ Drying   │
      └──────────┘
            │
     ┌────────────┐
     │ Calcination │
     └────────────┘
            │
      ┌──────────┐
      │ Powder   │
      └──────────┘
```

Figure 7: Flow scheme of the peroxide method.

particle size (<0.1 µm). After calcination at 900°C a powder with a specific area of 14 $m^2 \cdot g^{-1}$ and a particle size of 0.1 µm is obtained [26]. Sintering at 1400°C for 4 hours results in an increase of density from 47% to 97% [29].

An advantage of the peroxide method is that dopants can be introduced easily. The synthesis has been reported for powders doped with calcium, strontium, lead, zinc, cadmium, yttrium, aluminium, zirconium, manganese, tin, niobium, thallium, antimony and iron.

2.4.3 Dispersion

Dispersion methods are based on the atomisation of a precursor solution into small droplets. The various dispersion methods differ in the mechanism of precursor solution transformation into the intermediate droplet phase, which gives rise to a limitation of the distance across which phase separation can occur. This results in the formation of individual granular particles only. The resulting powders have limited agglomeration, but can have a high agglomerate strength. With this technique a number of specific preparation methods for barium titanate can be distinguished.
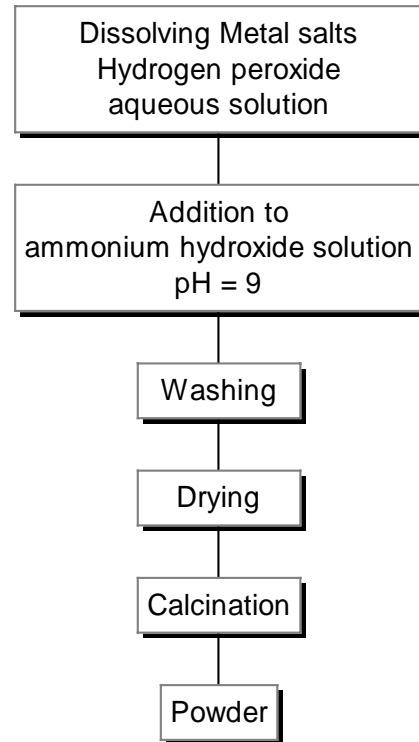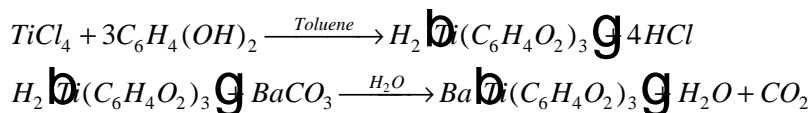
2.4.3.1 Freeze-drying

The freeze-drying method (sometimes referred to as cathecholate process) is reported to result in an ultrafine powder. The process starts with the reaction of $TiCl_4$ with cathegol (aromatic diol, $(C_6H_4(OH)_2)_2.4H_2O$) to form a titanium complex, see also *figure 8*. The complex reacts with $BaCO_3$ to form a water-soluble mixed cathegol complex. [30-32]

$$TiCl_4 + 3C_6H_4(OH)_2 \xrightarrow{\ Toluene\ } H_2 \left[Ti(C_6H_4O_2)_3 \right] 4HCl$$

$$H_2 \left[Ti(C_6H_4O_2)_3 \right] BaCO_3 \xrightarrow{\ H_2O\ } Ba \left[Ti(C_6H_4O_2)_3 \right] H_2O + CO_2$$

The resulting aqueous solution of the cathegol complex is freeze-dried. Freeze-drying is performed by spraying the salt solution in a cold solvent, followed by drying under vacuum and subsequent slow heating, while melting is avoided [30].

After freeze-drying, calcination occurs at 600°C. The primary particles are clustered into flake-like soft agglomerates. The maximum agglomerate size is 1-2 µm, the surface area is approximately 20 $m^2 \cdot g^{-1}$ and the aggregate size is lower than 0.1 µm.

Die-pressed compacts made from powders prepared by decomposing the cathegolate precursor at 600°C, reached a density of 95 % after 30 minutes sintering at 1270°C [30].

Figure 8: Flow scheme of the freeze drying method.

2.4.3.2 Liquid aerosol technique

The liquid aerosol technique (The technique is also referred to as: mist decomposition technique, aerosol decomposition, spray pyrolysis or spray roasting) is based on the thermal decomposition of barium and titanium complexes in air. The liquid aerosol technique has certain advantages:

- Easy control of particle size
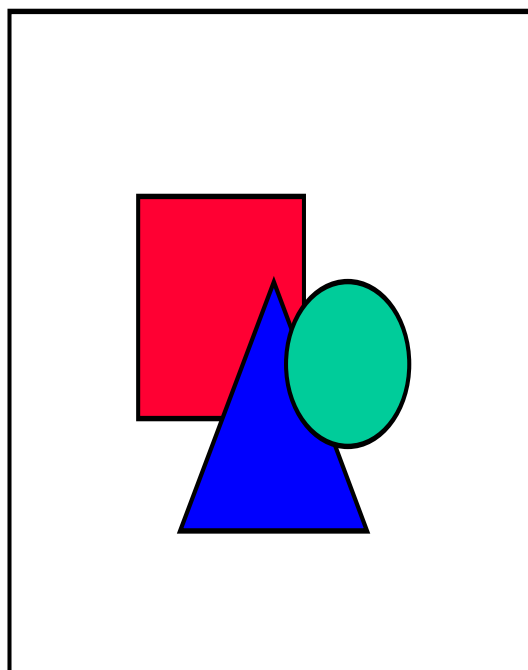- Preparation of spherical particles
- Narrow size distribution

The mist decomposition technique starts by dissolving titanium oxynitrate in water. To this solution hydrogenperoxide and acetylacetone are added. These chelating agents are both necessary to stabilise the aqueous titanium solution and are mixed with a solution containing the appropriate amount of barium [33].

The precursor solution is transformed to mist, which is lead through three ovens. In the first water is evaporated, in the second thermal decomposition of the inorganic salts occurs and in the third crystallisation takes place. Then the particles are collected by means of a glass filter. The method results in a single-phase tetragonal barium titanate powder.

The average grain size of the produced powder is 0.64 µm. The particles are polycrystalline and almost spherical. No densification data are available for this method.

2.4.3.3 Spraying in alcohol

In this dispersion method an aqueous solution of citrates and formates is sprayed into an alcohol. Each droplet results in essentially one powder particle. The precipitate is formed by dehydration of individual droplets in alcohol (alcohol drying). After precipitation at most 0.1 % of the relevant elements remain in solution [34].

The cationic hydroxides are dissolved in water with citric acid and ammonia. To limit the water content of the alcohol after precipitation, the aqueous solutions must be as concentrated as possible. Some solubility problems occur but at pH = 5 most of the citrate solutions are relatively stable (at least for a few hours). The solutions are sprayed into a ten- to twenty-fold volume of an alcohol [34]. The alcohol that is actually needed depends on the cation salt. To separate the precipitate from the liquid, the supernatant is decanted, followed by filtration. After this treatment, the powder is washed, dried and calcined at 800°C, resulting in formation of barium titanate. The particles have a size of 3 to 10 µm and are rod-shaped.

For sintering, the powder is pressed isostatically at 1.47 MPa. The product is then heated for two to four hours between 1300 to 1360°C in a stream of oxygen, which results in a density of 99%. A great advantage of this preparation method is the low carbon content of approximately 0.04 % [34].

2.5   Sol-Gel Method

The sol-gel preparation method starts with the production of a sol, which is converted by a gelation process into a gel. This gel can be calcined to result in a polycrystalline barium titanate powder. The sol-gel method is, in spite of the high production cost, increasingly used for the production of high technology ceramics, because sol-gel prepared powders have superior mechanical stability and a high chemical purity [35]. Unfortunately due to strong aggregation of fine particles, the sol-gel powders suffer generally from an unfavourable morphology. Therefore, attempts to fabricate dense ceramic bodies from sol-gel prepared powders led to disappointing results. Note that the preparation of thin ceramic layers with the sol-gel method is described extensively in literature [36-38].

Figure 9:   Flow scheme of a sol-gel method, with acetic acid.

In the gelation processes a resin is formed, similar to the resin formed in the prolysis preparation methods. Contrary to the complexation methods, in sol-gel processes the metal ions contribute significantly to the molecular network of the resin. Just like the pyrolysis methods no washing step is possible, so that (traces of) the used precursors must be removed by thermal decomposition.

The mechanism of the sol-gel processes is divided into two parts and described below.

1. Hydrolysis reaction, which consists of a nucleophilic attack of water on the metalorganic or metal-salt molecules present in solution [39], this results into the formation of a sol.

2. Polycondensation reaction, in which a 2- or 3-dimensional network is formed, usually of an amorphous structure [39].
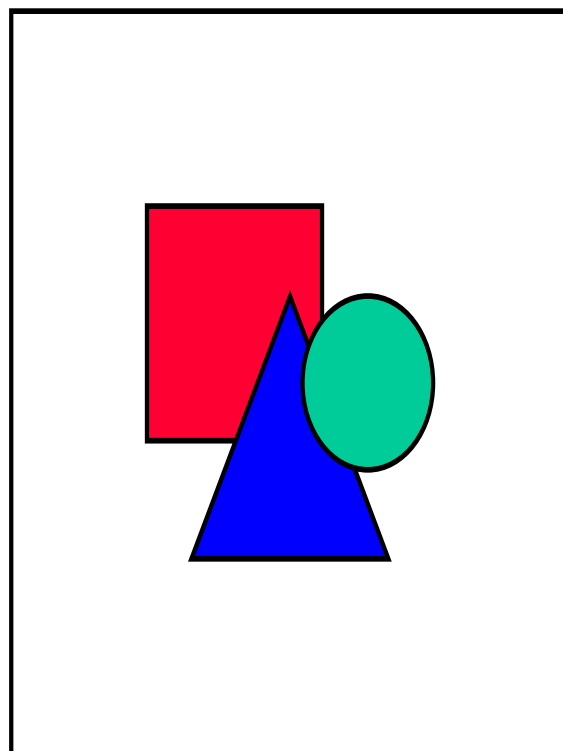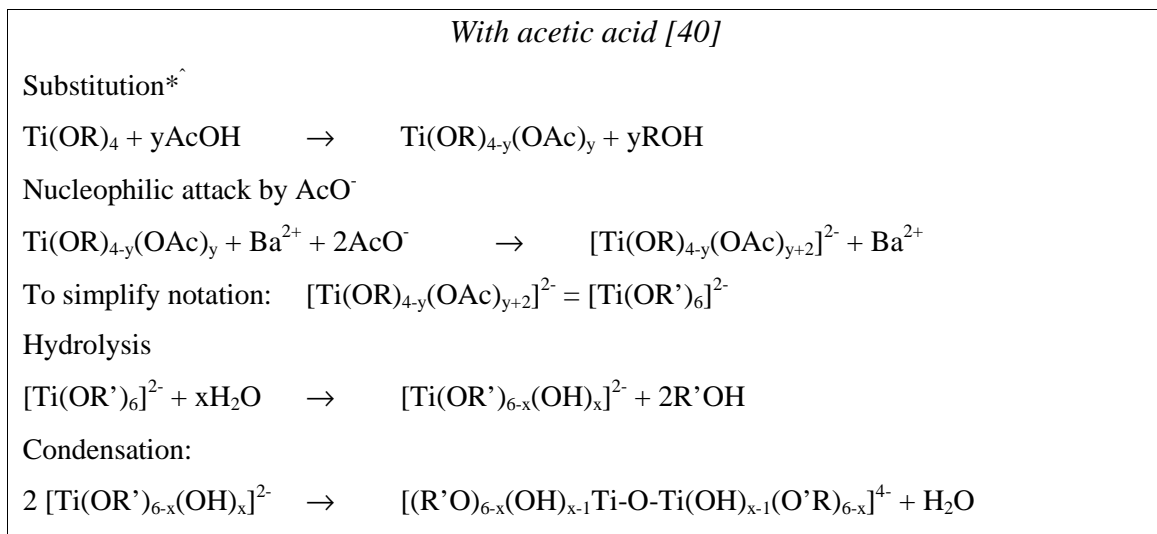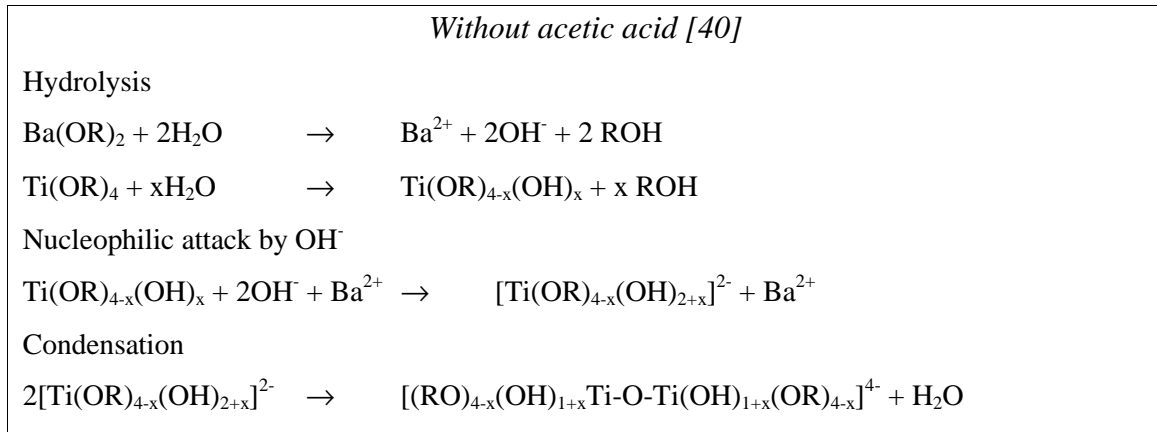

Without acetic acid [40]

Hydrolysis

$Ba(OR)_2 + 2H_2O \rightarrow Ba^{2+} + 2OH^- + 2 ROH$

$Ti(OR)_4 + xH_2O \rightarrow Ti(OR)_{4-x}(OH)_x + x ROH$

Nucleophilic attack by OH^-

$Ti(OR)_{4-x}(OH)_x + 2OH^- + Ba^{2+} \rightarrow [Ti(OR)_{4-x}(OH)_{2+x}]^{2-} + Ba^{2+}$

Condensation

$2[Ti(OR)_{4-x}(OH)_{2+x}]^{2-} \rightarrow [(RO)_{4-x}(OH)_{1+x}Ti-O-Ti(OH)_{1+x}(OR)_{4-x}]^{4-} + H_2O$

With acetic acid [40]

Substitution*ˆ

$Ti(OR)_4 + yAcOH \rightarrow Ti(OR)_{4-y}(OAc)_y + yROH$

Nucleophilic attack by AcO^-

$Ti(OR)_{4-y}(OAc)_y + Ba^{2+} + 2AcO^- \rightarrow [Ti(OR)_{4-y}(OAc)_{y+2}]^{2-} + Ba^{2+}$

To simplify notation: $[Ti(OR)_{4-y}(OAc)_{y+2}]^{2-} = [Ti(OR')_6]^{2-}$

Hydrolysis

$[Ti(OR')_6]^{2-} + xH_2O \rightarrow [Ti(OR')_{6-x}(OH)_x]^{2-} + 2R'OH$

Condensation:

$2 [Ti(OR')_{6-x}(OH)_x]^{2-} \rightarrow [(R'O)_{6-x}(OH)_{x-1}Ti-O-Ti(OH)_{x-1}(O'R)_{6-x}]^{4-} + H_2O$

2.5.1 Acetic acid

Powders prepared according to the sol-gel method are described schematically in *figure 9*. The powders prepared in the presence of acetic acid and calcined at 600°C have an average particle size of 5 µm [41]. A corresponding green compact with a density of 65% starts to densify at 1000°C. The densification is not yet complete at 1380°C. The density reaches a maximum of 95% by sintering at 1250°C for 4 hours.

2.5.2 Without Acetic acid

During the sol-gel preparation method in the absence of acetic acid, normally 2-methoxyethanol is added. The addition of 2-methoxyethanol has the effect that the titanium alkoxide groups are hydrolysed quickly and completely before the addition of

---

* This reaction is simplified because AcO can act as bidentate ligand too.

water. This allows polycondensation to take place which on its turn promotes the formation of a gel [36]. The gel consist of crystalline pseudo-cubic barium titanate particles with an average size of less than 50 nm. Powders prepared with a sufficiently high concentration of the precursor solution have a high sinterability [37]. Sintering of a green body starts below 900°C with a maximum densification rate at 1000°C. Sintering is complete at approximately 1100°C, after which the density has increased from 65% to 98%.

The reaction rate of the precursors in the sol-gel method depends on the amount of water and the action of a catalyst [38]. Unfortunately, the barium precursor is highly sensitive towards water and carbondioxide. The process has therefore to be conducted in a carbondioxide-free atmosphere. The sol-gel method is highly flexible, because of the large number of different alkoxide precursors available. By choosing suitable metal-organic precursors it is possible to use the preparation method to prepare sols, which can be used in dip coating or spin coating processes. Some modifications of the sol-gel preparation method are described in literature [39, 40]. Most of these methods are based on the replacement of the expensive and moisture-sensitive barium alkoxide precursors by less expensive inorganic barium salts.

2.6   Precipitation

Precipitation methods are mainly used for powders which consist of only a few elements. If more elements are required in the powder, it is difficult to obtain the desired stoichiometry owing to the differences in solubility of the various metal ions [42]. Precipitation methods commonly lead to the formation of small particles in solution. However, these small particles might form hard aggregates either during the precipitation process or during further processing steps, like filtration, washing, drying and calcination.

2.6.1   Direct precipitation

The direct precipitation is also referred to as the hydroxy preparation or the gel-precipitation method [9, 43-44]. This method is suitable for commercial powder preparation, since the use of inexpensive inorganic precursors lowers the manufacturing costs of the powders. Unfortunately, a carbondioxide-free atmosphere still has to be used to avoid formation of barium carbonate.

The direct precipitation method is based on the insolubility of barium and titanium ions in an aqueous environment at a high pH, as is shown in *figure 10*. The method starts by hydrolysis of a titanium precursor at pH 6-8, which results in the formation of a $TiO_2 \cdot xH_2O$ gel. The titanium precursors used for this method are titaniumtetrachloride, titanyl sulphate and titanium oxysulphate. The gel is washed in order to remove hydroxide and chloride ions. Next an aqueous solution containing barium ions is added. The barium solution can be prepared from either barium nitrate, barium hydroxide, barium chloride or barium acetate. The pH of the barium and titanium solution is increased by the addition of a base, normally ammonium hydroxide [45]. The mixture is heated for several hours after which the precipitate is filtered off and washed.

Important process parameters are the pH of the reaction mixture, which must exceed pH 13.5, the molar ratio between Ba and Ti, which must be in between 0.7 and 5 and, the reaction temperature, which must be higher than 40°C and preferably near the boiling temperature.

With the direct precipitation method $BaTiO_3$ powders have been produced with a uniform primary particle size as small as 20 to 30 nm. The powder produced according to the precipitation method is a cubic perovskite without second phases. However,
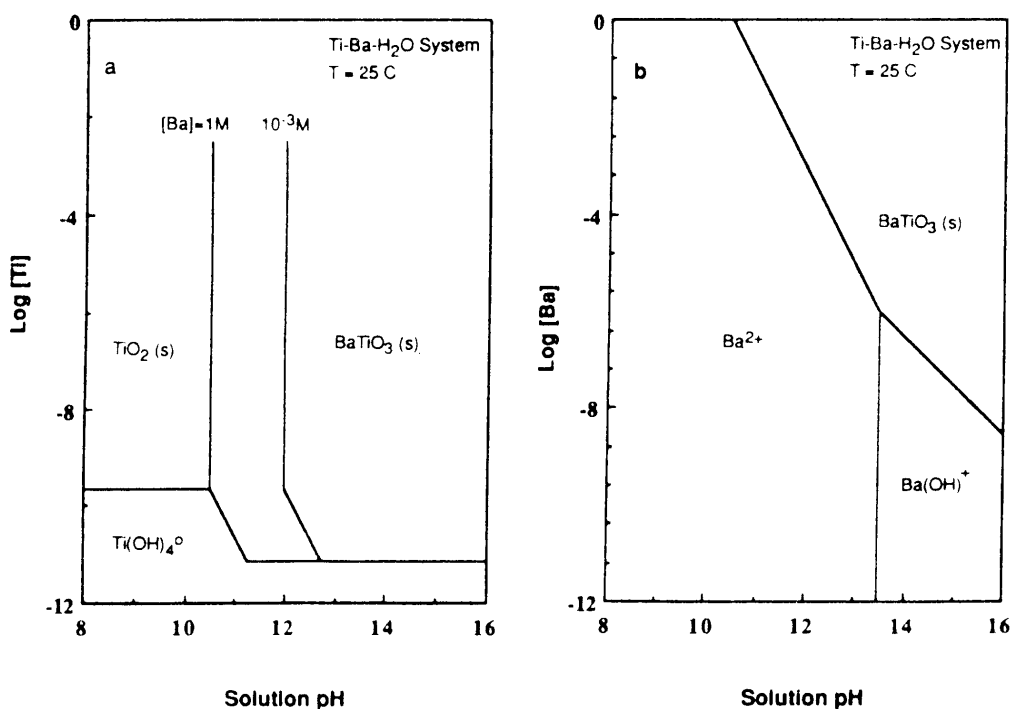
Figure 10: *log[Me]-pH diagrams for the Ti-Ba-H_2O system at 25°C, (a) log[Ti]-pH; (b) log[Ba]-pH [32].*

powders produced with the direct precipitation method consist of hard aggregates of 4 µm as measured with light scattering. In the calcined powder a titanium excess was established with XRF. Sintering at 1300°C results in a density increase from 45 to 80%. The low final density is attributed to the titanium excess and the hard aggregates, which creates irregular packing.

The direct precipitation method can also be used in combination with freeze-drying, see the corresponding paragraph in this chapter [46]. Ocaña et al. describe the continuous preparation of $SrTiO_3$, produced by the same reaction mechanism [44]. Hence it should also e possible to develop this method for the preparation of barium titanate.

2.6.2 Hydrolytic precipitation

The simultaneous hydrolytic decomposition of barium and titanium alkoxides was first described by Mazdiyasni [47]. The hydrolytic preparation method starts with a mixture of barium and titanium alkoxides dissolved in alcohol, followed by the addition of water, which hydrolyses the alkoxide precursors [47-50].

$$Ti(OR)_4 + 4H_2O + Ba^{2+} + 2\,OH^- \quad \rightarrow \quad Ti(OH)_6^{2-} + Ba^{2+} + 4\,ROH$$

$$Ti(OH)_6^{2-} + Ba^{2+} \quad \rightarrow \quad BaTiO_3 + 3\,H_2O$$
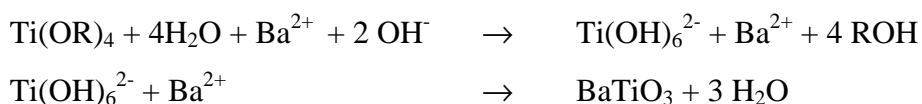
The process starts by dissolving titanium isopropoxide and either barium alkoxide or barium acetate in an organic solvent like isopropanol or benzene. The use of barium acetate is preferred because in that case the use of the moisture-sensitive and expensive bariumalkoxide is avoided. The solution is refluxed for several hours after which water is added dropwise. The precipitate is collected by filtration and dried at 50°C in a vacuum oven. The powder is calcined at 700°C for 2 hours [47].

An uncalcined powder produced with this method has a crystallite size of 50 to 150 nm and a maximum aggregate size smaller than 1 µm. The titanium over barium ratio of the calcined powder was 0.999 ±0.001 as measured with XRF. During sintering at 1375°C for 1 hour the density increased from 51% to 98% [47].

2.6.3 Hydrothermal preparation

In the hydrothermal preparation route, barium reacts under pressure with titania gels. The method is described first by Flaschen and might be interesting, because the formation of barium titanate takes place at low temperatures [51,52]. Therefore, the

calcination step can be avoided, and consquently the formation of highly agglomerated particles may be avoided too [53].

The process starts with titania or with reactive, freshly precipitated gels of hydrated titania and zirconia ($TiO_2.xH_2O$ + $ZrO_2.xH_2O$). The gel or the titania is mixed with a bariumhydroxide solution, which is pressurised and heated during which crystalline barium titanate particles are formed. The precipitate is subsequently washed and dried.

$$TiO_2 + Ba(OH)_2 \xrightarrow{p,T} BaTiO_3 (crystallite) + H_2O$$
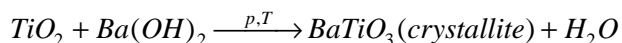
Important parameters in this process are the precipitation temperature and the choice of precursor [53, 38]. The average size of the powder particles as obtained with the hydrothermal method ranges from 0.04 to 0.11 µm when amorphous titania or from 0.2 to 0.7 µm for when crystalline (rutile) tiania is used [54].

The hydrothermal method has been applied for pure and zirconium-doped barium titanate as well as other compounds such as $CaTiO_3$, $SrTiO_3$ and $CdTiO_3$ [55,56]. The method has also been applied for the preparation of thin films of tetragonal barium titanate on a titanium metal substrate [57].

2.6.4   Sol-crystal

The sol-crystal method is based on crystallisation, rather than precipitation. In this method large single crystals of metal alkoxides are produced as an intermediate. This leads to a homogeneous distribution of metal ions at the atomic level and a well-defined stoichiometry in the resulting oxides at low temperatures.

The barium precursor ($Ba(O-i-Pr)_2$) is dissolved in isopropylalcohol or benzene and mixed with the titanium isopropoxide. The mixture is heated under argon to 45°C and stirred until everything is dissolved. Next, the mixing is stopped and than the solution is cooled and kept overnight at room temperature to form crystals. The crystal growth is continued for a few days. The method results in transparent crystals that have a square and platelike shape, which in case of benzene as solvent has the following composition: $BaTi(OiPr)_6 \cdot (C_6H_6)_x$. The size of the crystals varies from a few millimeters to 1 cm and their density is 1.64 g·cm^{-3}. The crystals can (partially) be converted to tetragonal barium titanate at temperatures as low as 150 to 800°C under an argon flow. Powders calcined at 800°C for 3 hours have a particle size up to 50 nm. The ratio [Ba]:[Ti] established with XRF is 1.03 ± 0.03 [58].

2.6.5 Electrochemical preparation

Electrochemical preparation is commonly used for the preparation of thin films. These thin films are either made by the deposition of barium on a titanium substrate or by the deposition of both barium and titanium on a steel substrate [57-59]. During deposition on a titanium substrate three processes play a role:

1. Rapid formation of either a titania or a titanium hydrous oxide film.

2. Nucleation of fine barium titanate crystallites on the surface of the amorphous metastable titania film and further growth to an insulating polycrystalline film of barium titanate.

3. If the voltage exceeds a critical value, dielectric breakdown of the films occurs, which is a process which interferes with processes 1 and 2 [59].

The electrochemical preparation starts by dissolving barium hydroxide or barium acetate in water at pH > 12.5. Prior to the anodic deposition on a titanium substrate, the solution is heated to 55°C. The apparatus used in electrochemical preparation is shown in *figure 11* [60]. After deposition, the precipitate is washed and finally dried. With the electrochemical preparation method, single phase barium titanate films can be prepared. For a deposition temperature of 55°C a film thickness of 1 µm was obtained.

Barium titanate films deposited on steel had to be calcined at temperatures around 800°C to obtain a pure polycrystalline barium titanate phase. With the electrochemical method it is possible to obtain a film with a titanium over barium ratio of around 1. It is also possible to change this ratio since the titanium over barium ratio can be controlled very well by the applied potential [61]. The method has been described for $BaTiO_3$,
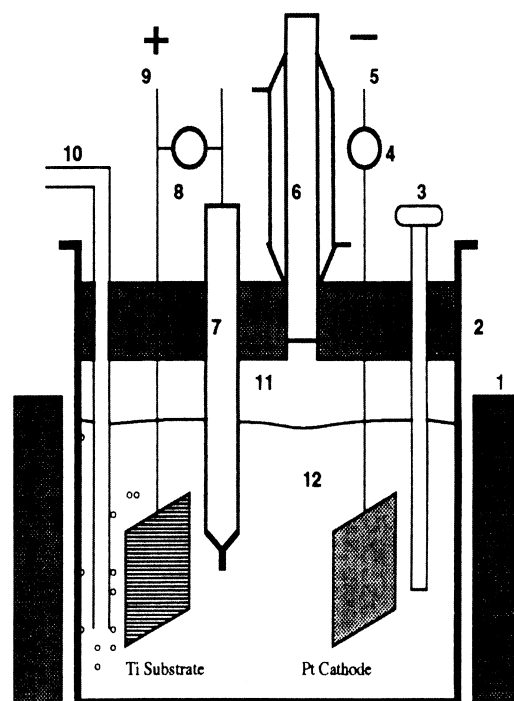

Figure 11:   Schematic diagram illustrating the experimental apparatus for electrochemical deposition, 1 heater, 3 thermocouple, 4 current recorder, 5 Pt cathode, 6 condenser tube, 7 Ag/AgCl reference electrode, 8 voltage recorder, 9 Ti anode, 10 gas inlet, 12 electrolyte solution.

LaMnO$_3$, LaCo$_3$ and LaCrO$_3$. Note that Schlenkrich et al. mention that the preparation of BaZrO$_3$ films is not successful [62].

2.7 General considerations

The amount of literature on barium titanate preparation is overwhelming and this survey can, therefore, not be complete. Because the choice of preparation method depends on the application, some examples of barium titanate are summarised together with the most suitable preparation method. Barium titanate can be, amongst others, applied in:

- **Bulk ceramics** (e.g. as lamp starter); For this type the preparation method must be above all cheap. The mixed oxide method is a good choice. When improvements are required in e.g. the chemical homogeneity or sinterability, a wet-chemical preparation method may be applied, preferably a precipitation or complexation-precipitation method, which starts with chloride precursors. Both these methods are relatively inexpensive.

- **Thin layers** (e.g. MLCC's); The morphology of the powder becomes more important for this type of application. But on the other hand production costs may also not be too high. Again precipitation or complexation-precipitation methods are the most suitable. Note that the complexation-precipitation techniques can be used in combination with dispersion techniques, homogeneous precipitation (see chapter 5 of this thesis) or emulsion technology. The latter is based on reactions in (micro)emulsions in which the size of the reactors is very small. Consequently very small and homogeneous particles can be prepared with this method [63]. The precipitation of barium titanate by (micro) emulsion technology is not yet described in literature.

- **High technology applications**; Here no limitations exist in the production costs, therefore the sol-gel method is a good option. If a dense ceramic is required, however, other techniques, like pyrolysis-based complexation techniques might be more effective.

References

1. G. Aliprandi, M. Alvazzi Delfrate, V. Buscaglia, M. Leoni and P. Nanni, "Influence of additives on the sintering of BaTiO$_3$ prepared from different routes," pp. 793-98 in *Third*

Euro-Ceramics 1, Proceedings of the European Ceramic Society. Edited by G. de With, R.A. Terpstra and R. Metselaar, European Ceramic Society, Maastricht, the Netherlands, 1993.

2. S. Kumar and G.L. Messing, "Synthesis of barium titanate by a basic pH Pechini process," pp. 95-100 in *Better ceramics through chemistry V*, Proceedings of the Materials Research Society Symposium (San Fransisco, CA, April, 1992). Edited by M.J. Hampden-Smith, W.G. Klemperer and C.J. Brinker. Materials Research Society, Pittsburgh, PA, 1992.

3. S. Uedalra, H. Yamanoi and H. Tamura, "Methods of manufacturing metal titanate fine powders," *EP Patent no. 0,104,002*, August 24 1983.

4. M.P. Pechini, "Method to prepare lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor," *US Patent no. 3,330,697*, July 11 1967.

5. "Werkwijze ter bereiding van keramische materialen op basis van gemengde oxyden," *Nl patent no. 6,903,840*, September 16 1969.

6. G. Tomadl, H. Rösch and A. Stiegelschmitt, "Preparation of $BaTiO_3$ by sol-gel-processing," pp. 281-85 in *Better ceramics through chemistry III*, Proceedings of the Materials Research Society Symposium (Reno, Ne, April, 1988). Edited by C.J. Brinker, D.E. Clark and D.R. Ulrich. Materials research Society, Pittsburgh, PA, 1988.

7. P.P. Phule and S.H. Risbud, "Review; Low-temperature synthesis and processing of electronic materials in the $BaO-TiO_2$ System," *J. Mat. Sci.*, **25** (1990) 1169-83.

8. M.R.F. Kuntz, "Development and optimization of precursor materials for solid oxide fuel cells by the nitrate pyrolysis process (NPA)," pp. 301-12 in Proc. 3th Int. Symp. of precursor materials for solid-fuel cells (1993).

9. M. Ocaña and C.J. Serna, "Continuous production of spherical strontium titanate at low temperature," *J. Mat. Sci. Lett.*, **9** (1990) 772-73.

10. S.L. Peschke, M. Ciftcioglu, P.H. Doughty and J.A. Voight, "Preparation of strontium titanate powders for decomposition of polymeric precursors," pp. 101-06 in *Better ceramics through chemistry V*, Proceedings of the Materials Research Society Symposium (San Fransisco, CA, April, 1992). Edited by M.J. Hampden-Smith. Materials Research Society, 1992 Pittsburgh, CA, 1992.

11. N.C. Eror and H.U. Anderson, "Polymeric precursor synthesis of ceramic materials"; pp. 571-77 in *Better ceramics through chemistry II,"* Proceedings of the Materials Research Society (Palo Alto, CA, April, 1986). Edited by C.J. Brinker, D.E. Clark and D.R. Ulrich. Materials Research Society, Pittsburgh, PA, 1986.

12. N.-K. Kim, H.-S. Kim and G.-S. Lee, "Effect on sintering atmosphere on the properties of Ceria-doped barium titanate," pp. 1915-18 in *Euro-Ceramics II*, Proceedings of the 2nd Int. Conf. on Electroceramics and Ceramics for Special Applications (Augsburg, FRG, September, 1991). Edited by G. Ziegler and H. Hausner. Deutsche Keramische Gesellschaft, Köln, FRG, 1991.

13. J. Reuterty, O. Wittke and G.J. Piderit, "Polyitacornates in the Pechini synthesis of mixed ceramics oxides," pp. 1885-1889 in *Euro-Ceramics II*, Proceedings of the 2nd Int. Conf. on Electroceramics and Ceramics for Special Applications, (Augsburg, FRG, September, 1991). Edited by G. Ziegler and H. Hausner. Deutsche Keramische Gesellschaft, Köln, FRG, 1991.

14. P.A. Lessing, "Mixed-cation oxide powders via polymeric precursors," *J. Am. Ceram. Soc. Bull.*, **68** [5] (1989) 1002-07.

15. G. Guldnet, S. Merklein and D. Sporn, "Sol-gel processing of functional ceramic layers," pp. 2357-61 in *Euro-Ceramics II*, Proc. 2nd Int. Conf. on electroceramics and ceramics for special applications (Augsburg, September, FRG, 1991). Edited by G. Ziegler and H. Hausner. Deutsche Keramische Gesellschaft, Köln, FRG, 1991.

16. D. Hennings and W. Mayr, "Thermal decomposition of (BaTi) citrates into barium titanate," *J. Solid State Chem.*, **26** (1978) 329-38.

17. J.A.M. van Roosmalen, E.H.P. Cordfunke and J.P.P. Huijsmans, "Sinter behaviour of $(La,Sr)MnO_3$," *Solid State Ionics*, **66**, (1993) 285-293.

18. R.H.E. van Doorn, H. Kruidhof, L. Winnubst, H.J.M. Bouwmeester and A.J. Burggraaf, "Preparation of perovskite ceramics by decomposition of metal-EDTA Complexes," *Submitted for publication*.

19. H-.W. Wang, D.A. Hall, F.R. Sale, "Phase homogeneity and segregation in PZT powders prepared by thermal decomposition of metal-EDTA complexes derived from nitrate and chloride solutions," *J. Am. Ceram. Soc.*, **75** [1] (1992) 124-30.

20. H-.W. Wang, D.A. Hall, F.R. Sale, "Effects of metal salts on the thermal decomposition of EDTA-gel precursors for ferroelectric ceramic powders," *J. Thermal Anal.* **42** (1994) 823-38.

21. X. Wang, C. Zhao, Z. Wang, F. Wu and M. Zhao, "Synthesis of $BaTiO_3$ nanocrystals by stearic acid gel method," *J. Alloys and Comp.*, **204** (1994) 33-36.

22. K. Kudaka, K. Iizumi and K. Sasaki, "Preparation of stoichiometric barium titanyl oxalate tetrahydrate," *Ceram. Bull.*, **61** (1982) 1136.

23. H. Yamamura, A. Wanatabe, S. Shirasaki, Y. Moriyoshi and M. Tanada, "Preparation of barium titanate by oxalate method in ethanol solution," *Ceramics Inter*. **11** [1] (1985) 17-22.

24. K. Osseo-Asare, F.J. Arriagada and J.H. Adair, "Solubility relationships in the coprecipitation synthesis of barium titanate: heterogeneous equilibria in the Ba-Ti-C_2O_4-H_2O system," pp 47-53 in *Ceramic transactions*, Edited by G.L. Messing, E.R. Fuller Jr. and H. Hausner, Proceedings of the fist international conference on powder processing science, Orlando, USA, (1987).

25. M. Murata and A. Kitao, "Preparation of titanates," *Us patent no.* 4,061,583 December 6 (1977).

26. G. Pfaff, "Preparation and characterization of titanate powders of different sinterability," *J. Mat. Sci.*, **27** (1992) 1222-26.

27. G. Pfaff, "Herstellung von $BaTiO_3$-Sinterpulver durch Fällung von $BaTiO_2$ $(O_2).3H_2O$," *Z. Chem.*, **28** [2] (1988) 76-77.

28. G. Pfaff, "Synthesis and Charaterization of $BaTi_4O_9$," *J. Mat. Sci. Lett.*, **10** (1991) 129-31.

29. G. Pfaff, "Synthesis and Charaterization of $BaTi_2O_5$," *J. Mat. Sci. Lett.*, **9** (1990) 1145-47.

30. A.J.A. Winnubst, "Chapter; Wet chemical preparation methods," pp. 9-43 in *Preparation and properties of Oxidic Ceramic Powders*. Enschede, 1993.

31. N.J. Ali and S.J. Milne, "Synthesis and properties of barium titanate powder derived from a cathechol complex," *Br. Ceram. Trans. J.*, **86** (1987) 1113-17.

32. N.J. Ali and J. Bultitude, L.A. Xue and S.J. Milne, "Preparation of stoichiometric $M'TiO_3$ powders (M' = Ba, Sr, Ca) from cathecholate complexes"; pp. 269-74 in *Better ceramics through chemistry III*, Proceedings of the Materials Research Society symposium (Reno, Ne, April, 1988). Edited by C.J. Brinker, D.E. Clark and D.R. Ulrich. Materials Research Society, Pittsburgh, PA, 1988.

33. S. Wada, A. Kubota, T. Suzuki and T. Noma, "Preparation of barium titanate fine particles from chelated titanium and barium nitrates by the mist decomposition in air," *J. Mat. Sci. Lett.*, **13** (1994) 190-93.

34. B.J. Mulder, "Preparation of $BaTiO_3$ and other ceramic powders by coprecipitation of citrates in alcohol," *Am. Ceram. Soc. Bull.*, **49** [11] (1970) 990-93.

35. D. Hennings, "Review of chemical preparation routes for barium titanate," *in British ceramics proceedings*, (1989) 1-10.

36. C. Lemoine, B. Gilbert, B. Michaux, J.-P. Pirard and A.J. Lecloux, "Synthesis of barium titanate by the sol-gel process," *J. Non-crystalline solid*, **175** (1994) 1-13.

37. H. Shimooka, M. Kuwabara, "Preparation of dense BaTiO3 ceramics from sol-gel derived monolithic gels," *J. Am. Ceram. Soc.*, **78** [10] (1995) 2849-52.

38. P.P. Phule and S.H. Risbud, "Review low-temperature synthesis and processing of electronic materials in the BaO-TiO_2 system," *J. Mat. Sci.* **25** (1990) 1169-83.

39. M.H. Frey and D.A. Payne, "Synthesis and processing of barium titanate ceramics from alkoxide solutions and monolithic gels," *Chem. Mater.* **7** (1995) 123-29.

40. F. Chaput and J.P. Boilot, "Chemically derived Ba titanate gels and ceramics," in *High Tech. Ceram.*, Edited by P.Vincenzini, Elsevier, Amsterdam (1987) 1459-68.

41. J. Retuert, O. Wittke and G.J. Piderit, "Polyitaconates in the Pechini synthesis of mixed ceramic oxides," pp 1885-1889 in *Euro-Ceramics II*, Proc. 2nd Int. Conf. on electroceramics and ceramics for special applications (Augsburg, September, FRG, 1991). Edited by G. Ziegler and H. Hausner. Deutsche Keramische Gesellschaft, Köln, FRG, 1991.

42. S. Uedalra, H. Yamanoi, H. Tamura, "Methods of manufacturing metal titanate fine powders," *EP Patent no. 0,104,002*, August 24 1983.

43. D. Völtzke, T. Langhammer and H.-P. Abicht, "Bariumtitanat-Pulver nach der Hydroxid-Methode," *Silikattechnik*, **39** [2] (1988) 63-64.

44. "Werkwijze ter bereiding van keramische materialen op basis van gemengde oxyden," *Nl patent no. 6,903,840*, September 16 1969.

45. M. Kahn, "Preparation of small grained and large-grained ceramics from Nb-doped BaTiO$_3$," *J. Am. Ceram. Soc.*, **54** [9] 452-54 (1971).

46. G. Pfaff, "Wet chemical synthesis and characterization of barium titanate sintering powders"; pp. 1879-83 in *Euro-Ceramics II*, Proc. 2nd Int. Conf. on electroceramics and ceramics for special applications (Augsburg, September, FRG, 1991). Edited by G. Ziegler and H. Hausner. Deutsche Keramische Gesellschaft, Köln, FRG, 1991.

47. K.S. Mazdiyasni, R.T. Dolloff, and J.S. Smith II, "Preparation of high-purity submicron barium titanate powders," *J. Am. Ceram. Soc.*, **52** [10] (1969) 523-26.

48. K.S. Mazdiyasni, "Fine particle perovskite processing," *Ceram Bull.*, **63** [4] (1984) 591-94.

49. M.H. Frey and D.A. Payne, "Synthesis and processing of barium titanate ceramics from alkoxides solutions and monolithic gels," *Chem. Mater.,* **7** (1995) 123-29.

50. R.N. Viswanath, S. Ramasamy, K. Shanmugam and R. Ramamoorthy, "Preparation and characterization of nanocrystalline BaTiO$_3$," *J. Mater. Sci.,* **14** (1995) 841-43.

51. A. Nordlund Christensen, "Hydrothermal preparation of barium titanate by transport reactions," *Acta Chemica Scand.*, **24** (1970) 2447-52.

52. S.S. Flaschen, "An aqueous synthesis of barium titanate," *J. Am. Ceram. Soc.*, **77** (1995) 194 .

53. C.T. Xia, E.W. Shi, W.Z. Zhong, J.K. Guo, "Preparation of BaTiO$_3$ by the hydrothermal method," *J. Eur. Ceram. Soc.,* **15** (1995) 1171-76.

54. H. Kuwmazawa, T. Kagimoto, A. Kawabata, "Preparation of barium titanate ultrafine particles from amorphous titania by a hydrothermal method and specific dielectric constants of sintered discs of the prepared particles," *J. Mater. Sci.*, **31** (1996) 2599-2602.

55. R. Vivekanandan, S. Philip and T.R.N. Kutty, "Hydrothermal preparation of Ba(Ti,Zr)O$_3$ fine powders," *Mat. Res. Bull.*, **22** (1986) 99-108.

56. N. Yasuda, T. Kato, T. Hirai, M. Mizuno, K. Kurachi and I. Taga, "Dielectric properties of BaTiO$_3$, Sr- and Pb-substituted BaTiO$_3$ ceramics synthesized through hydrothermal method," *ferroelectrics*, **154** (1994) 331-36.

57. K. Kajiyoshi, N. Ishizawa and M. Yoshinmura, "Preparation of tetragonal barium titanate thin film on titanium metals substrate by hydrothermal method," *J. Am. Ceram. Soc.*, **74** [2] (1991) 369-74.

58. Y. Suyama and M. Nagasawa, "Synthesis of single-crystal barium isopropoxide complex to form barium titanate," *J. Am. Ceram. Soc.*, **77** [2] (1994) 603-05.

59. T. Watari, K. Shigematsu, T. Torikai, and O. Matsuda, "Preparation and properties of BaTiO$_3$ films by electrophoretic deposition," *Electroceramics IV*, Aachen, Germany (1994) 353-56.

60. Y. Matsumoto. T. Morikawa, H. Adachi, and J. Hombo, "A new preparation method of barium titania perovskite film using electrochemical reduction," *Mat. Res. Bull.,* **27** (1992) 1319-27.

61. P. Bendale, S. Venigalla, J.R. Ambrose, E.D Verink, and J.H Adair, "Preparation of barium titanate films at 55°C by an electrochemical method," *J. Am. Ceram. Soc.,* **76** [10] (1993) 2619-27.

62. F. Schlenkrich and M. Eber, "Preparation of thin films of titanates and zirconates by a electrochemical-hydrothermal method," *Electroceramics. IV*, Aachen, Germany (1994) 351 4.

63. W. Sager, H.-F. Eicke and W. Sun, "Precipitation of nanometer-sized uniform ceramic particles in emulsions," *Coll. Surf. A: Phys. Eng. Asp.*, **79** (1993) 199-216.

3. An oxalate-peroxide complex used for the preparation of doped barium titanate [*]

Abstract

A method for the preparation of homogeneously-doped barium titanate, which can be applied in non-linear dielectric elements is described. Barium and titanium salts are mixed with hydrogen peroxide and added to a solution of ammonium oxalate, resulting in the precipitation of $BaTi_{0.91}Zr_{0.09}O_2(C_2O_4).2H_2O$. The presence of oxalate ions and a high pH are necessary to obtain stoichiometric, sinter-active powders. The decomposition of the complex is studied by means of d-TGA and FTIR. Sintering of the green compacts results in a density of 96%.

3.1 Introduction

Doped barium titanate is used in a broad range of electroceramic devices. One example is its use in lamp starters in fluorescent lamps as starter pulse-generating device [1]. For such an application non-linear dielectric behaviour is essential. The required material properties for this type of application are: a high dielectric constant, a steep gradient of the polarisation versus the electric field hysteresis curve and stable non-linear characteristics. These specifications can be met when the ceramic devices are made with a sinteractive, homogeneous Zr-doped barium titanate powder [1-3]. Nowadays, doped barium titanate powders are mainly produced commercially by the mixed oxide process. The powders made by this route have certain disadvantages, like a large and non-uniform particle size and also low chemical homogeneity. However, the mixed oxide process is easy to perform and when evaporation is avoided, stoichiometric powders can easily be obtained. An improvement in homogeneity and morphology of the powder can be obtained when wet-chemical routes are utilised. This development will also lead to better dielectric behaviour. Unfortunately, during wet-chemical

---

[*] This chapter was published as a paper in *J. Mater. Chem.*, **8** (5) (1998) 1251-54.

preparation all kinds of undesired side reactions may occur, which makes control of the stoichiometry more complicated.

An already existing commercial wet-chemical preparation route is the oxalate process [4,5]. In this process pure, undoped barium titanate is produced stoichiometrically by the formation and precipitation of a barium-titanium-oxalate complex at low pH and a temperature of 60°C.

A different process for the preparation of barium titanate is a reaction based on the formation and the precipitation of a titanium peroxide complex at high pH and room temperature [6]. This process has not only been described for barium titanate, but also for the production of titanium-rich materials ($BaTi_2O_5$) as well as barium zirconates and calcium and magnesium-titanates [6-10]. However, both the peroxide and the oxalate methods were not used for the preparation of Zr-doped $BaTiO_3$ powders until now. The process described in this chapter is a combination of both processes and suitable for the production of Zr-doped-barium titanate ($BaTi_{0.91}Zr_{0.09}O_3$). Doping seems possible due to the simultaneous presence of hydrogen peroxide and ammonium oxalate.

To obtain the appropriate dielectric properties deviations from the desired composition must be minimised and a dense ceramic is also required. These demands are fulfilled best when the powders are sinteractive. This means that the presence of aggregates in the powder must be prevented while the powder should have a small average grain size. In contrary, the grain size of the final ceramic must be large because large grains reduce internal stress. On its turn a low amount of internal stress results in better non-linear dielectric properties [11].

3.2. Experimental procedure

3.2.1 Powder and ceramic preparation

Titanium oxychloride (0.15 mol; 0.076 M) and zirconium chloride (0.015 mol; 0.0076 M) are added to nitric acid in water (0.2 M). This mixture is mixed with an aqueous solution of barium nitrate (0.17; 0.042 M), prepared from barium carbonate and nitric acid. Finally, to this solution hydrogen peroxide is added. This so-called "precursor" solution is slowly added to a solution which is prepared from ammonium

hydroxide (0.35 mol) and different amounts of oxalate acid. In this paper the ratio of oxalate ion concentration over the concentration of all metal ions (Ba+Ti+Zr) present in solution, is called *x (0≤x≤0.5)*. All experiments are performed at room temperature. After two hours stirring, the obtained precipitate is filtered, washed with ethylacetate, dried at 150°C and calcined at 900°C.

Powders are pre-pressed uniaxially at 80 MPa and subsequently isostatically pressed at 400 MPa. All compacts (except the ones for dilatometer experiments) are sintered at 1400°C for 5 hours; heating rate $2°C \cdot min^{-1}$ and cooling rate $4°C \cdot min^{-1}$.

3.2.2 Characterisation

The decomposition of the dried precipitate was studied with TGA (Stanton Redcraft STA 625, heating rate $5°C \cdot min^{-1}$ to 1000°C) and Fourier-transform infra-red spectroscopy (FTIR). FTIR measurements were performed in situ at temperatures from 200 to 800°C at temperature intervals of 20°C (holding time = analysis time: few minutes).

XRD measurements were performed using a Philips PW 1710 with-filter CuKα1, λ=1.4508 Å. The chemical composition was measured with X-ray fluorescence (XRF, X-ray spectrometer, Philips PW 1480/10).

Particle size volume distribution was measured with a Microtrac X-100 (Leeds and Northrup). The morphology of the powder and the microstructure of the ceramic were studied with Scanning Electron Microscopy (Jeol, JSM 35CF at 15 kV). The microstructure of the ceramics is revealed by etching at a temperature 30°C below the sintering temperature in a nitrogen atmosphere. To study the influence of the ligand structure of the complex, the difference in absorption maximum, of a solution containing titanium and hydrogen peroxide at pH = 4, before and after the addition of oxalic acid was measured. UV/VIS-measurements were done with a Philips PU 8740.
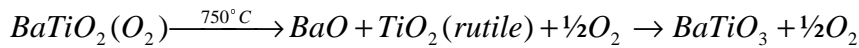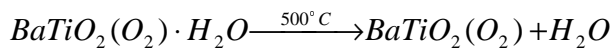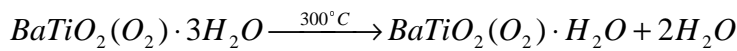
Non isothermal densification was studied with a Netzsch 410 dilatometer with a heating rate of $2°C \cdot min^{-1}$ and a cooling rate $4°C \cdot min^{-1}$ and a holding time of 3 hours. Density measurements were performed with the Archimedes technique using mercury.

3.3.   Results and discussion

The complexation starts with the addition of a red-coloured aqueous solution of titanium, zirconium, barium and hydrogen peroxide to a solution of ammonium oxalate. This results in the direct formation of a yellow precipitate. During the reaction gas-formation is observed, probably oxygen which is formed by the decomposition of hydrogen peroxide in the basic aqueous environment.

3.3.1   Identification of the formed complex

The weight loss of the dried precipitates, after heating the precipitates in the TGA to a temperature of 1000°C, for $x=0$ is 20%. This corresponds to the theoretical weight loss found for the thermal decomposition of $BaTiO_2(O_2) \cdot 3H_2O$ to $BaCO_3$. $BaTiO_2(O_2) \cdot 3H_2O$ is the complex formed with the peroxide method ($x=0$). The decomposition of this complex can be explained as follows [6]:

$$BaTiO_2(O_2) \cdot 3H_2O \xrightarrow{300°C} BaTiO_2(O_2) \cdot H_2O + 2H_2O$$

$$BaTiO_2(O_2) \cdot H_2O \xrightarrow{500°C} BaTiO_2(O_2) + H_2O$$

$$BaTiO_2(O_2) \xrightarrow{750°C} BaO + TiO_2(rutile) + \tfrac{1}{2}O_2 \rightarrow BaTiO_3 + \tfrac{1}{2}O_2$$

The first indication that the ligand structure changes in the presence of oxalate ions ($x>0$) in acidic environment is the shift of the absorption maximum of the complex from 356 nm in the absence of oxalate to 392 nm in the presence of oxalate, as measured with UV/VIS-spectroscopy. Note, that a titanium species formed by hydrolysis in an acidic aqueous environment will react with hydrogen peroxide in water to form the $Ti_2O_5^{2-}$ ion [12].

When oxalate is introduced in the process, the weight loss increases to 31% for $x = 0.5$. This weight loss can be explained by the decomposition of $BaTi_{0.91}Zr_{0.09}O_2(C_2O_4) \cdot 3H_2O$ into $BaTiO_3$. This complex is comparable to the complex obtained from the peroxide synthesis however the peroxo ligand has been exchanged by an oxalate ligand.

In *figure 1* the derivatives of the TGA (d-TGA) results are given for three precipitates prepared with $x = 0.125$, $x = 0.25$ and 0.50. It can be seen that with an increasing amount
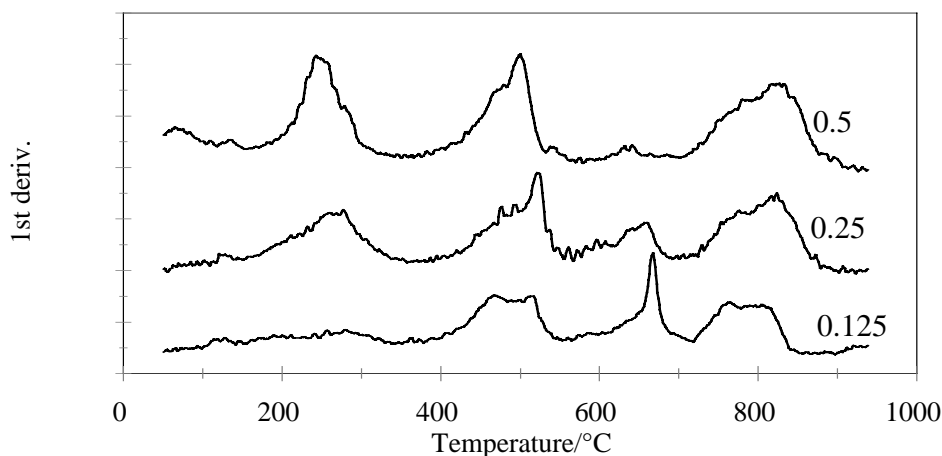
Figure 1:   *d-TGA of dried precipitate prepared with an increasing amount of oxalate, x (0.125, 0.25 and 0.5).*

of oxalate in the reaction mixture the d-TGA signals change especially at approximately 250°C and 700°C.

FTIR of the complex prepared in the presence of oxalate ($x = 0.5$), is measured in situ as a function of temperature in the range of 1000 - 4000 cm^{-1}. The spectra for $x = 0.5$ are given in *figure 2*. The IR signal labelled "1" (at 3500 cm^{-1}) corresponds to water. It is clearly visible that water is still present at temperatures up to 600°C. Most of the water is removed at temperatures between 400 and 500°C. Due to the gradual release of water this release is not visible in the plot of the derivative of the d-TGA-signal as given in *figure 1*.

The signal labelled "2" in *figure 2* (1700 cm^{-1}, other characteristic signal [14] at 1300 cm^{-1} is present but is not visible in this plot) corresponds to CO vibrations of the complex [13] $BaTi_{0.91}Zr_{0.09}O_2(C_2O_4)\cdot 3H_2O$. These vibrations have disappeared at 500°C indicating that this initial complex is no longer present this temperature.
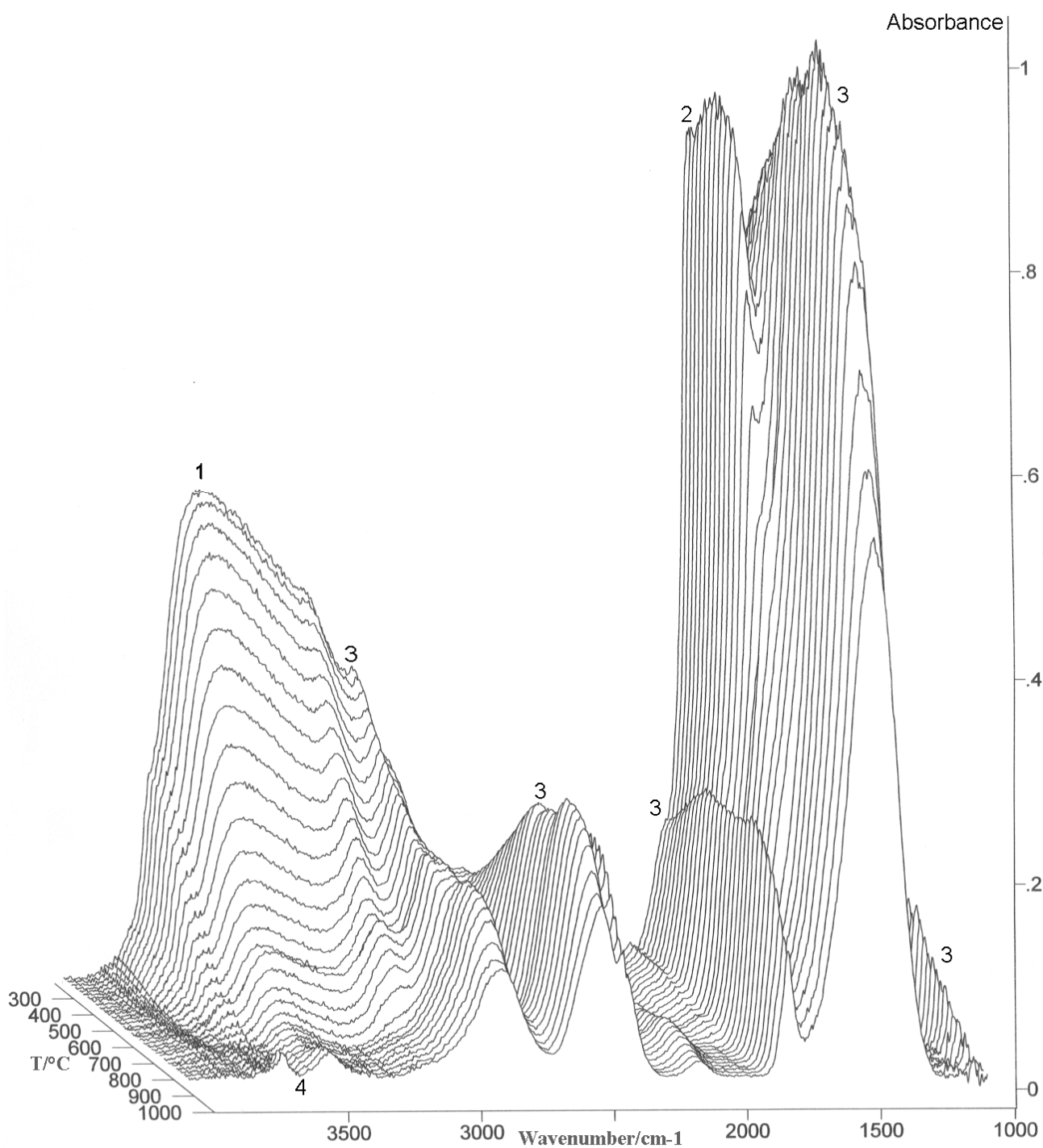
Figure 2: Infra-red spectra of the decomposition of the peroxo-oxalate complex (temperature intervals 20°C), x = 0.5. 1: water, 2: complex, 3: BaCO₃, 4: Ti(OH)ₓ.

Peaks marked by "3" (2500, 1750, 1500 and 1050 cm^{-1}) are attributed to CO vibrations in (barium)carbonate [13,14]. The intensity of these signals first increases and reaches a maximum at 600^oC. These vibrations are still present at 800^oC. Finally, the signal marked "4" (3550 cm^{-1}) corresponds tot OH vibrations of $Ti(OH)_x$ [14]. This signal arises at temperatures above 700^oC. All these FTIR data indicate that the initial complex decomposes to an intermediate which contains $BaCO_3$. XRD analysis indicates the onset of crystalline perovskite formation at 800^oC. So it can be concluded that the intermediate starts to decompose at this temperature.

FTIR analysis at 800^oC still shows the presence of $BaCO_3$. This was confirmed by XRD in which perovskite $BaTiO_3$ as well as $BaCO_3$ signals were found after heating at 800^oC. XRD analysis of a powder calcined at 900^oC showed a 100% perovskite crystal structure. The absence of bariumcarbonate at 900^oC could not be confirmed by infra-red because the maximum temperature for the high-temperature FTIR equipment used is 800^oC. The presence of a perovskite structure could also not be confirmed by these
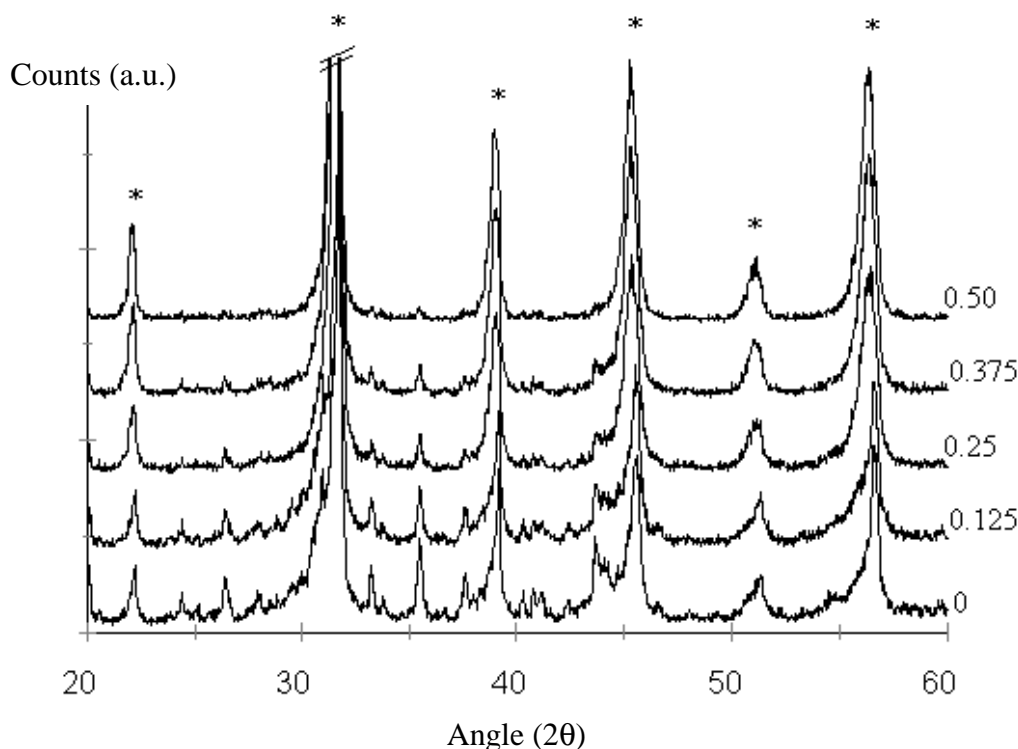
Figure 3:   XRD of calcined powder prepared with an increasing amount of oxalate, x, * denotes the (cubic) perovskite structure.

FTIR analysis because the infra-red perovskite signals are only present at relatively low wavenumber (< 1000 cm^{-1}) [13].

Using the combined data of TGA, FTIR and XRD measurements the following decomposition mechanism of the original complex is proposed:

$$BaTiO_2(C_2O_4) \cdot 3H_2O + O_2 \xrightarrow{250^\circ C} [BaCO_3 \cdot TiO_2.H_2O] + CO_2 + 2H_2O$$

$$[BaCO_3 \cdot TiO_2 \cdot H_2O] \xrightarrow{500^\circ C} [BaCO_3 \cdot TiO_2] + H_2O$$

$$[BaCO_3 \cdot TiO_2] \xrightarrow{800^\circ C} BaTiO_3 + CO_2$$
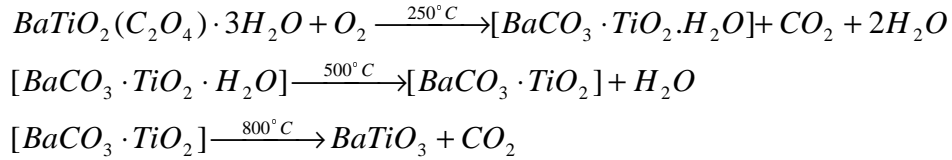
In these reactions Zr is left out for reasons of simplicity. It can be assumed that in this case Zr reacts in the same manner as Ti.

The temperatures correspond to the maxima in the d-TGA spectrum for $x = 0.5$ as can be seen in *figure 1*. Also considering the FTIR and XRD data these temperatures can be regarded as an onset temperature for these reactions.

3.3.2 Influence of oxalic acid on powder properties

In f*igure 3* XRD results are shown of the calcined powders prepared with an increasing oxalate content. It is clearly visible that the amount of second phase in the calcined powder as determined with XRD, depends on the oxalate concentration (x). For increasing amounts of oxalate, the amount of second phase decreases. The second phases present are mainly $BaTi_2O_5$ and $BaCO_3$. At 0.50 molar equivalent oxalate no second phases are present and only the cubic perovskite $BaTiO_3$ phase is present.

A second indication of the influence of oxalic acid on the power properties can be obtained with XRF. With an increasing oxalate concentration the Ba/(Ti+Zr) ratio of the calcined powder becomes closer to 1. For $x = 0.5$, the Ba/(Ti+Zr) ratio of the powder is 1.00 ± 0.01.

Table 1: Effect of the oxalate concentration on the aggregate size and green density.

Oxalate ratio, x	average aggregate size (μm)	green density (%)
0	7	55
0.125	5	58
0.25	4	59
0.375	3	60
0.5	1	67

The presence of ammonium oxalate also has influence on the powder morphology. An increase in the oxalate concentration leads to a decrease in aggregate size (see *table 1*). This decrease in aggergate size leads to an increase of the green density, also shown in *table 1*.

Apparently, the presence of oxalate in the precipitation step of the peroxo-oxalate process results in a different way of complex formation and decomposition.

A powder calcined at 900°C results in the formation of a single phase cubic perovskite. In *figure 4* a micrograph of this calcined powder ($x = 0.5$) is given. It is clearly visible that the powder consists

021009 15KV X25.0K 1.20um
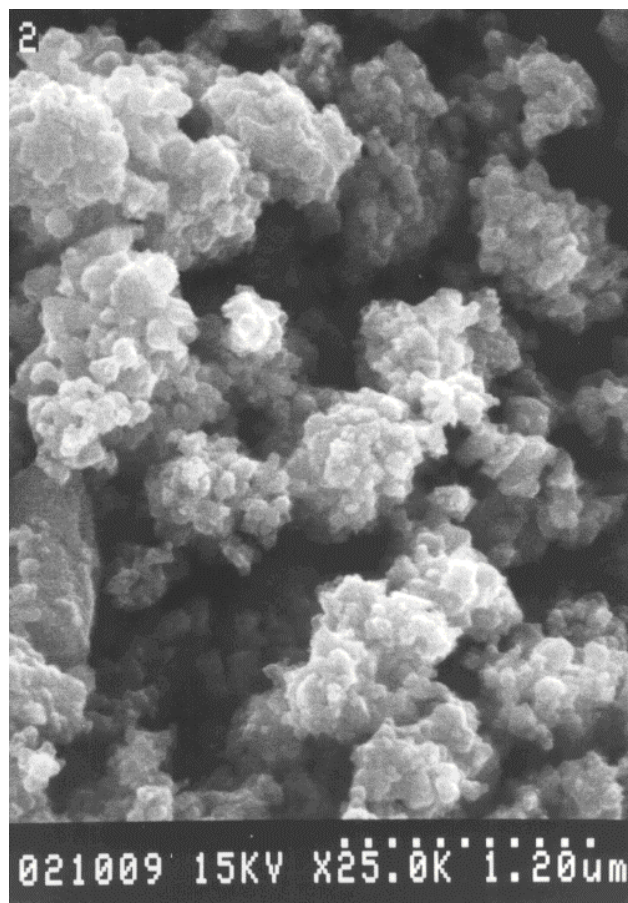
Figure 4:   SEM of calcined powder,x=0.5.

of agglomerates, which in their turn consist out of aggregates. The aggregate size obtained with SEM is comparable to the size determined with light scattering and shown in *table 1*. XRF showed an A/B ratio of 1.00 for *x* = 0.5, likewise no deviations are found for the ratio Zr to Ti.

TEM-EDX measurements are used to study the homogeneity of the material. TEM-EDX revealed that the composition of the particles remained constant for 10 selected particles, which is an important indication that the powder is homogeneous.

3.3.3   Densification

Dilatometer experiments on an isostatically pressed sample reveal a dense (96% rel. density) sample at a temperature of 1400°C. The maximum densification rate is approximately at 1180°C. A sample sintered for 10 hours at 1400°C has a grain size of 62 μm. Note that the high sintering temperatures were necessary to obtain a large grain size. Dielectric measurements results in an ε_r value of 27000 at a temperature of 90°C. At 70 and 110°C the dielectric constant has 20% of its maximum value.

3.4   Conclusions

The use of the modified peroxide method results in the formation of a homogeneous, sinteractive powder. To obtain a stoichiometric powder the use of oxalate in the process is essential. The precipitating-complex formed in this process is $BaTi_{0.91}Zr_{0.09}O_2(C_2O_4)\cdot 3H_2O$. The presence of oxalate not only allows the stoichiometric introduction of dopants, but improves the compaction behaviour as well.

References

1.   S. Iwaya, H. Masumura, Y. Midori, Y. Oikawa and H. Abe., "Non-linear polycrystalline barium titanate-type dielectric element," US Patent 4,404,029, 1983.
2.   D. Hennings and A. Schnel, "Diffuse ferroelectric phase transitions in $Ba(Ti_{1-y}Zr_y)O_3$ ceramics," *J.Am.Ceram. Soc.,* **65** [11] 539-44 (1982).
3.   S.M. Neirman, "The curie-point temperature of $Ba(Ti_{1-x}Zr_x)O_3$," *J. Mater. Sci.,* **23** 3973-80 (1998).
4.   M. Stockenhuber, H. Mayer and J.A. Lercher, "Preparation of barium titanates from oxalates," *J. Am. Ceram. Soc,* **76** [5] 1185-90 (1993).
5.   H. Yamamura, A. Watanabe, S. Shirasaki, Y. Moriyoshi and M. Tananda, "Preparation of barium titanate by oxalate method in ethanol solution ceramics international," *Ceram. Int.,* **11** [1] 17-22 (1985).

6. G. Pfaff, "Herstellung von BaTiO₃-Sinterpulver durch Fallung von BaTiO₂(O₂).3H₂0," *Z. Chem.*, **28** [2] 76-77 (1988).

7. G. Pfaff, "Synthesis and characterization of BaTi₂O₅," *J. Mater. Sci. Lett.*, **9** 1145-47 (1990)

8. G. Pfaff, "Chemical synthesis of calcium stannates from peroxo precursors," *Mater. Sci. Eng. B,* **33** 156-61 (1995).

9. G. Pfaff, "A novel reaction path to barium zirconates by the decomposition of peroxide precursors," *Mater. Lett.,*.**24** 393-97 (1995).

10. G. Pfaff, "Synthesis of magnesium stannates by thermal decomposition of peroxo-precursors," *Thermochim. Acta,* **237** 83-90 (1994).

11. D. Hennigs, "Barium titanate based ceramic materials for dielectric use," *Int. J. High Tech. Ceramics,* **3** 91-111 (1987).

12. J. Muhlebach, K. Muller and G. Schwarzenbach, "The peroxo complexes of titanium," *Inorg. Chem.*, **9**, 2381-90 (1970).

13. The sadtler standrad spectra, Sadtler research laboratories, Philadelphia (PA) USA.

14. G. Busca, V. Buscaglia, M.Leoni and P. Nanni, "Solid-state and surface spectroscopic characterization of BaTiO₃ fine powders," *Chem. Mater.*, **6** 955-61 (1994).

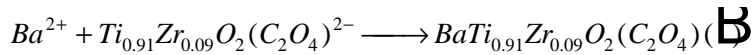# 4. Peroxo-oxalate preparation of doped barium titanate

Abstract

The peroxo-oxalate complexation method can be used for the preparation of doped barium titanate. This chapter is focussed on $BaTi_{0.91}Zr_{0.09}O_3$, which can be used as a discharge capacitor in lamp starters. The preparation method of the barium titanate powder, described in this chapter, is based on the complexation and subsequent precipitation in a basic environment of Ba, Ti and Zr ions with hydrogen peroxide and oxalate. To find optimal powder properties the influence of several process parameters, like precipitation temperature and pH, on powder properties is described. A single-phase perovskite crystal structure can be obtained, starting from a chloride precursor solution at a precipitation temperature of 40°C and a pH of 9.

4.1 Introduction

Doped barium titanate is used in a broad range of electroceramic devices. One example is a pulse-generating device as applied in lamp starters [1]. For such an application, a high dielectric constant, a steep gradient of the polarisation versus electric field hysteresis curve and stable non-linear characteristics are required. Those demands can be met by replacing around 9% of the Ti atoms in the perovskite lattice by Zr [2-5]. Doping with this amount of Zr results in a shift in phase transitions as a function of temperature. This shift in phase transition temperature results in the overlap of the three phase transitions, i.e. cubic-tetragonal, tetragonal-orthorhombic and orthorhombic-rhombohedric, see *figure 1*. Next to composition, chemical homogeneity and the presence of mechanical stress are important too, see also chapter 7. A higher degree of homogeneity results in a higher dielectric constant at the Curie-temperature [6,7]. A reduction in the amount of stress gives rise to a less diffuse phase transition, which results in a higher dielectric constant [5]. The amount of stress in the ceramic is reduced by the presence of large grains [5]. Therefore, the presence of large grains and consequently high sintering temperatures are required.

Nowadays, polycrystalline Zr-doped barium titanate for commercial application is prepared by the mixed oxide method [1,2]. The mixed oxide method is based on solid state reactions. Powders prepared by a solid state reaction unfortunately have a low chemical homogeneity [10]. To increase the homogeneity of powders and the derived ceramics, wet-chemical preparation techniques have to be used in stead of mixed oxide [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 which has reacted with hydrolysed titanium. The precipitate is thermally decomposed by calcination to $BaTi_{0.91}Zr_{0.09}O_3$ according to the following mechanism:

$$Ba^{2+} + Ti_{0.91}Zr_{0.09}O_2(C_2O_4)^{2-} \longrightarrow BaTi_{0.91}Zr_{0.09}O_2(C_2O_4)(B)$$

$$BaTi_{0.91}Zr_{0.09}O_2(C_2O_4)(B) + \tfrac{1}{2}O_2 \xrightarrow{T} BaTi_{0.91}Zr_{0.09}O_3 + 2CO_2(A)$$
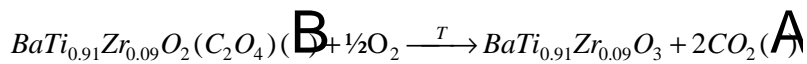
In this chapter the effect of the precipitation temperature, pH and choice of titanium and zirconium precursor on the powder properties is discussed in order to find the ideal process conditions for the preparation of Zr-doped $BaTiO_3$. Process conditions were
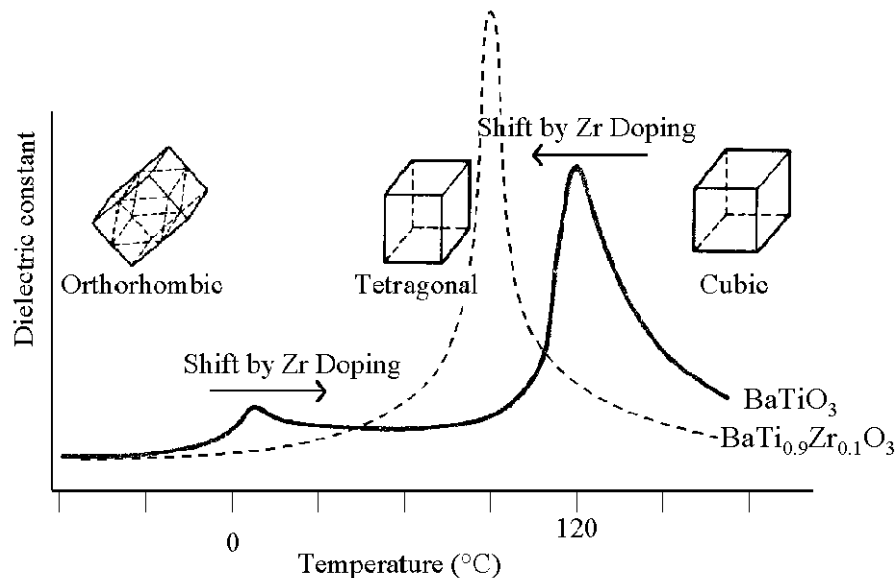

Figure 1:   Schematic diagram of the dielectric properties of pure and Zr-doped barium titanate.

optimised until a homogeneous, stoichiometric and sinteractive powder was obtained to be used for fabrication of a discharge capacitor.

4.2   Experimental Procedure

Two types of Zr and Ti precursor solutions are used.

- In the first experiments alkoxide precursors, Ti-isopropoxide and Zr-n-propoxide (70 wt% in n-propanol) are used.

- The second preparation process starts with titanium oxychloride and zirconium chloride.

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

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

One experiments with alkoxide precursors is conducted where the pH ranged from 4 to 10. The pH was adjusted by adding the appropriate amount of ammonium hydroxide to an aqueous solution of oxalic acid. All other experiments were conducted at pH 9. To ensure complete complexation and precipitation after addition of the precursors, the solution is stirred for 2 hours at the precipitation temperature. The precipitate is separated from the solution by filtration, washed with water to remove chloride ions, washed with ethylacetate to decrease the agglomerate strength, dried at 150°C, ball-milled in isopropanol and finally calcined at 900°C for 5 h. with a heating and cooling rate of 5°C·min^{-1}.

Ceramics are obtained by pre-pressing uniaxially at 80 MPa and subsequently isostatically pressed at 400 MPa. All compacts are sintered in air for 5 h at 1400°C. with heating and cooling rates of 2 and 4°C·min^{-1}, respectively.

4.2.1 Characterisation

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

Crystal structures are revealed by XRD, using a Philips PW 1710 with-filtered Cu Kα1, λ=1.4508 Å. The chemical composition of the calcined powders is measured by XRF using an X-ray spectrometer Philips PW 1480/10.

Particle size distribution is measured with a Microtrac X-100 in a diluted aqueous environment (Leeds and Northrup). For data analysis it is assumed that the powders are completely reflecting and spherical. The morphology of the powder is studied with Field Emission Scanning Electron Microscopy (Hytachi, type S800).

The microstructure of polished ceramic samples is revealed by thermal etching in a nitrogen atmosphere at 1370°C, followed by sputtering with gold. The microstructure is studied with Scanning Electron Microscopy (Jeol, JSM 8500).

Non-isothermal densification is studied with a Netzsch 410 dilatometer. The heating rate is 2°C·min^{-1}, the cooling rate 4°C·min^{-1} and the holding time 3hours at a temperature of 1400°C. Density measurements are performed with the Archimedes technique, using mercury.

4.3 Results and discussion

4.3.1 Influence of pH

The effect of pH on the complexation and the precipitation was studied by varying the pH in the range of 4-10 at room temperature using Ti- and Zr-alkoxide as precursors. In literature high and low pH conditions are used in respectively the peroxo and the oxalate precipitation processes for the preparation of barium titanate [11,12]. It can be

---

*   Ti-isopropoxide and Zr-n-propoxide (70 wt% in n-propanol) were obtained from Aldrich, Zwijndrecht, The Netherlands, all other chemicals were obtained from Merck, Darmstadt, Germany.
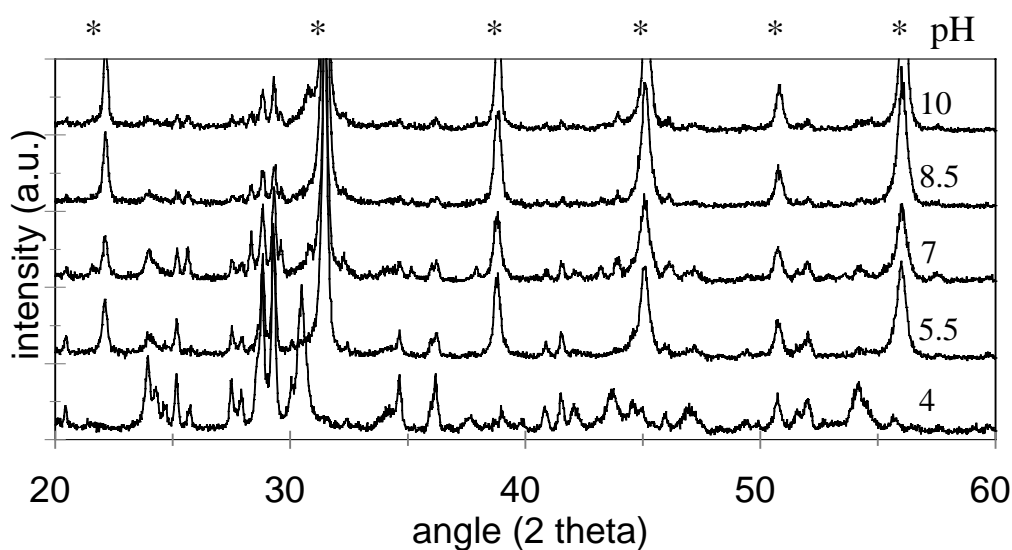
Figure 2: *XRD of calcined powders prepared out of an alkoxide precursor at different pH's, precipitation temperature 20°C. * Indicates perovskite BaTiO₃.*

seen in *figure 2* that the amount of second phases decreases drastically when the pH is increased. XRD measurements show no difference between the calcined powders prepared at pH 8.5 and at pH 10. A small amount of titanium-peroxo complex in aqueous solution results in a red colour [9], the change in colour of the filtrate from red at pH 4.5 to colourless at pH 8.5 and 10 indicates that at low pH titanium-peroxo complexes remain in solution too.

The pH effect of the solution can be explained by the fact that at a high pH, $Ti_{0.91}Zr_{0.09}(O_2)(C_2O_4)^{2-}$ is formed [8]. This complex is thermally more stable than the complex without oxalate [13]. This complex reacts with barium and precipitates stoichiometrically. At low pH another complex similar to $Ti(O_2)OH^+$, which does not precipitate with barium, is formed [10]. Therefore, the titanium complex remains in solution and is subject to condensation. Due to the presence of hydrogen peroxide and in spite of the presence of oxalate at low pH, the titanium complex is in such a form that the titanium-peroxo complex as well as the barium ions will remain in solution.

Note that the difference in complexation and precipitation behaviour between the peroxo-oxalate process and the commercial oxalate process, which is used for the preparation of undoped barium titanate, can be explained by the presence of hydrogen peroxide. The structure of the complex changes from $BaTi_{0.91}Zr_{0.09}O_2(C_2O_4).3H_2O$ to

$BaTiO(C_2O_4)_2.4H_2O$ for the oxalate method. Due to this change in complex structure the precipitation behaviour of the titanium oxalate complexes changes too.

4.3.2 Influence of precipitation temperature, alkoxide precursors

To study the effect of temperature on the complexation properties of oxalate, precipitation experiments were performed in a temperature range from 0 to 80°C at pH 9. In *figure 3* the XRD results of calcined powders, prepared by precipitation at different precipitation temperatures are given. It is clear that precipitation at 60°C leads to a powder with the smallest amount of second phase. At a precipitation temperature of 80 °C a considerable amount of $BaTi_2O_5$ and a third phase, $BaCO_3$ is formed.

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

- Hydrolysis of Zr- and Ti-precursor (alkoxide or oxychloride), which takes place around pH 3. It is expected that $BaCO_3$ is dissolved directly as Ba^{2+} after the addition of nitric acid.

- Complexation of the titanium and zirconium species with hydrogen peroxide after hydrolysis. At low pH, complexes like $Ti(O_2)OH^+$ are present in solution [11].

- Change in complex structure by addition of the precursor solution to the ammonium oxalate solution. Due to the change in pH from 3 to 9 and the presence of hydrogen peroxide and oxalate, the structure of the complex changes to $Ti_{0.91}Zr_{0.09}O_2(C_2O_4)^{2-}$ [8]. Therefore, the formation of the precipitating complex can be described as follows:

$$Ba^{2+} + Ti_{0.91}Zr_{0.09}O_2(C_2O_4)^{2-} + 3H_2O \longrightarrow BaTi_{0.91}Zr_{0.09}O_2(C_2O_4)\cdot 3H_2O$$
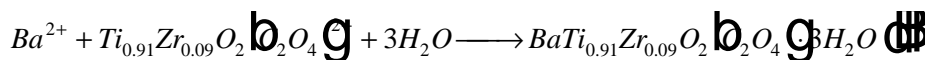
- Condensation of Zr and Ti-components. Condensation reactions occur both at high and low pH. Which condensation products are formed depends on the pH. At pH <3 $TiO_3(H_2O)_x$ is formed. At a higher pH $Ti_2O_5(OH)_2^{(2-x)+}$ is formed, which is a compound that can condensate to poly-nuclear titanium compounds and finally to peroxo-titanium hydrate $((TiO_3 \cdot (H_2O)_x)$ [11]. Condensation is an undesired side reaction, which leads to titanium and zirconium rich phases in the powder. Therefore, to obtain a homogenous powder condensation should be avoided.
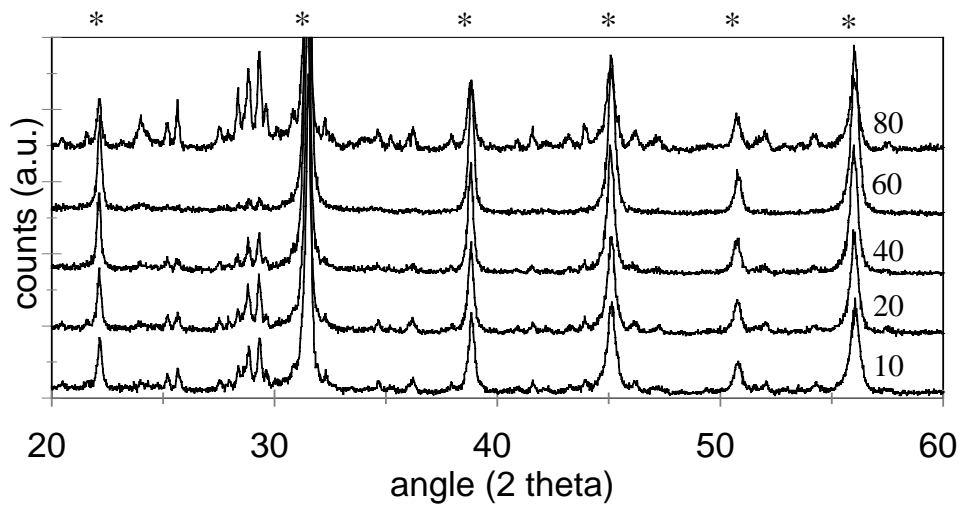
Figure 3:   *XRD results of calcined powders prepared from an alkoxide precursor at pH 9 at different precipitation temperatures. * indicates perovskite BaTiO$_3$ phase.*
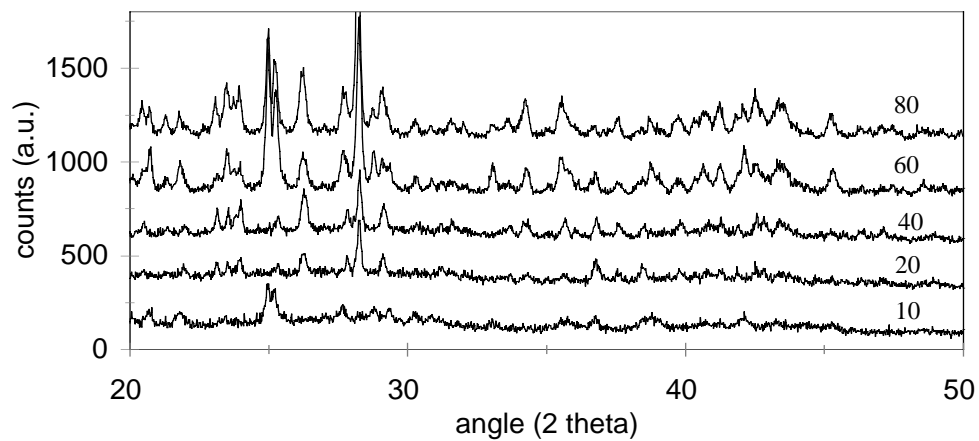

Figure 4:   *XRD results of uncalcined powder prepared from a chloride precursor at different precipitation temperatures.*

•

At low precipitation temperatures, the hydrolysis of the titanium and zirconium-isopropoxide proceeds rather slowly. Directly after addition of the precursor to water a white precipitate was formed, which dissolves very slowly. When the precursor solution was added to the ammonium oxalate solution and consequently the pH was raised from 3 to 9, the structure of the titanium-peroxo complex changes as described above. When incomplete hydrolysis has occurred, other species than $Ti_{0.91}Zr_{0.09}O_2(C_2O_4)^{2-}$ will be formed. It is also possible that the complexation with oxalate and hydrogen peroxide is not complete. 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 hydrolysed but due to the high precipitation temperatures, more and faster condensation will take place. Condensation processes lead to the formation of second phases, in this case both a titanium-rich and a barium-rich phase are formed [11].

Precipitation at 60°C results in the most homogeneous powder, but second phase formation can not be avoided completely when the process is started with titanium and zirconium alkoxides.

4.3.3   Influence of precipitation temperature, the chloride precursors

In *figure 4* the XRD spectra of the uncalcined powders, prepared from chloride precursors at pH 9 are given. In this figure it is visible that some crystallinity is present before calcination. The intensity and therefore the amount of the crystalline phase increases with increasing precipitation temperature. The XRD pattern of the main phase present in the uncalcined powders is comparable to barium oxalate [18-0203], with the most intense peak 25°2θ. 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 none of the signals an exact fit with reference spectra could be made. However, the presence of a species similar to barium oxalate is obvious for all precipitation temperatures. The presence of this oxalate species indicates the presence of the peroxo-oxalate complex. The reason why in the two cases a different hydrate is formed is not clear, small changes in the drying step may account for this.
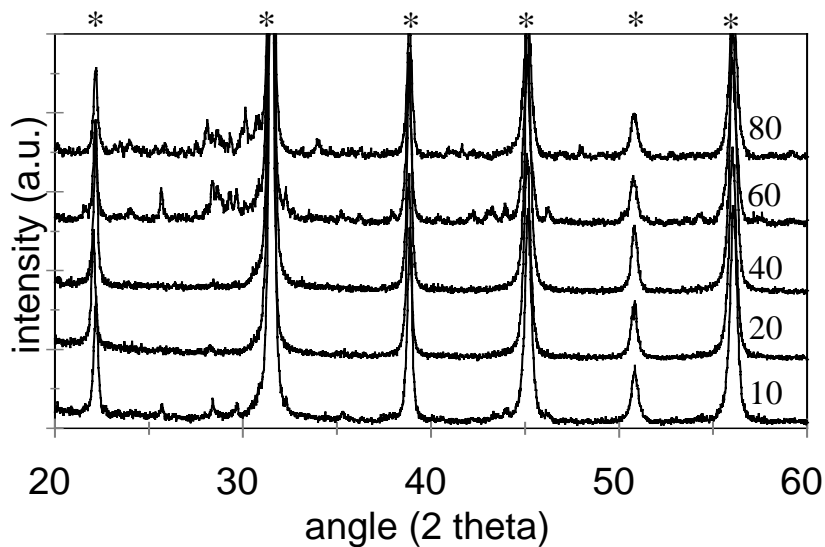
Figure 5: XRD results of calcined powders prepared out of a chloride precursor at pH 9 at different precipitation temperatures.

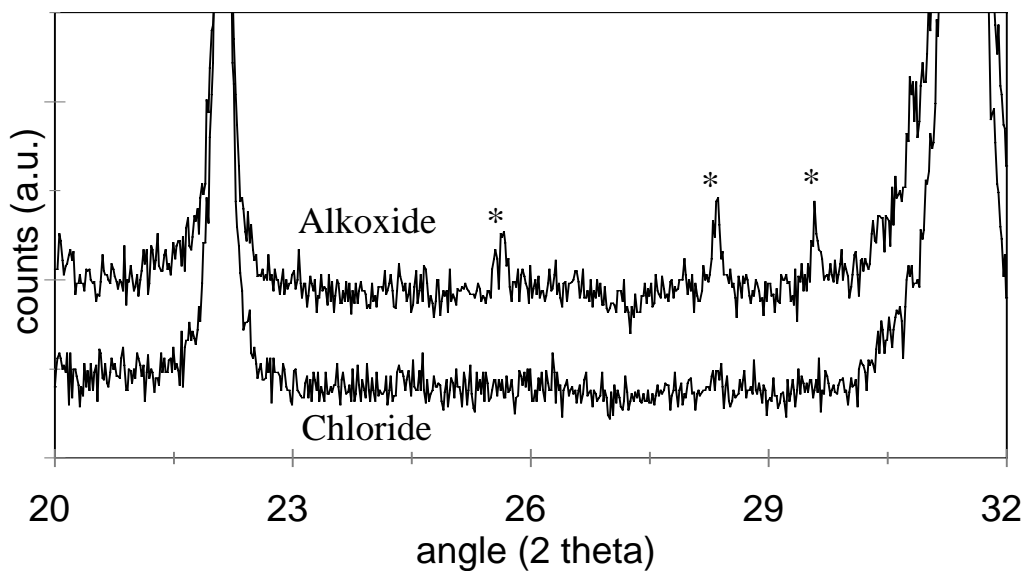*Figure 6: XRD of calcined powders prepared from a chloride precursor and a alkoxide precursor, precipitation temperature 20°C,* Indicates second phase.*

Table 1:   Density before and after sintering of compacts prepared from powders precipitated at different temperatures. Sintering conditions: heating and cooling rate 2°C.min^{-1}; sintering temp. 1400°C; time 5 h.

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

Figure 5 shows the diffraction data of the calcined precipitates prepared in a temperature range of 10 to 80°C. It is clearly visible that no or an insignificant amount of 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 than the amount of second phases found for the calcined power prepared at a precipitation temperature of 10°C.

The second phases present in the calcined powders, mainly consist of $BaTi_2O_5$ and $BaCO_3$. The mechanism for the 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 the starting chloride will either not be hydrolysed fully or the ligand exchange of the peroxoligand with the oxalate is incomplete. Both mechanisms will lead to the formation of second phases.

In *table 1* the green and final density of compacts prepared at different precipitation temperatures are given. 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 at 40°C has the highest density. 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.

XRF measurements indicate that the hydrolysis and condensation reactions only have influence on the second phase formation of the powder but not on the final composition

Table 2:   *Molar ratios of elements as measured with XRF corresponding to various processing steps. Process parameters: precipitation temperature 20°C, chloride precursor and pH = 9.*

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

of the calcined powder, see *table 2*. Precipitation at 20-40°C results in the most homogeneous powder.

4.3.4   Influence of the type of precursor

The advantage of the use of an alkoxide instead of a chloride as precursor is the fact that only organic matter has to be removed from the precipitate, which can easily be done during calcination. Chloride ions can not be removed during calcination but they have to be removed by washing. The presence of chloride ions in the precipitate will furthermore result in the formation of a $BaCl_2$ liquid phase during sintering [10]. To prevent this impurity effect, chloride ions have to be removed completely.

As is visible in *figure 6*, the XRD spectra of both calcined powders are given. Both samples are prepared under the same reaction conditions, precipitation at 20°C and at pH 9. It is clearly visible that the powder prepared from the alkoxide precursor contains some second phase, which consist of $BaTi_2O_5$. This is also visible in *figures 4* and *5*. Clearly smaller amounts of second phases are formed when chloride precursors are used. XRF indicates that the calcined powders prepared from the different precursors have the same composition.

It can therefore be concluded that for both systems complete precipitation occurs. In case of the use of chloride precursors this precipitate and also the calcined powder are more homogeneous.

The difference in amount of second phases can be explained by the difference in hydrolysis rate of both precursors. Titanium chloride hydrolyses immediately in water [11]. During addition of the alkoxides to diluted nitric acid it was clearly visible that the hydrolysis of titanium and zirconium alkoxides is much slower. This has the conse-

quence that complexation with barium, hydrogen peroxide and oxalic acid will take place slower and will be incomplete.

4.3.5 General discussion

From the results described above it can be derived that for the peroxo-oxalate process chloride precursors have to be used at pH 9 and a temperature of approximately 20 to 40°C. To be able to control the stoichiometry of the calcined powder, it is necessary to measure the concentration of the elements in each processing step. In *table 2*, the ratios of the elements are given as measured in the various processing steps. The process is described for a chloride precursor at 20°C and pH 9. It was found that no variation in the concentration 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 and neither to the formation of second phases, even when the precursor solution was poured directly into the ammonium oxalate solution. This indicates that the complexation and precipitation proceed fast.

After calcination the powders are wet-milled in isopropanol. From 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 measuring error.

Another important parameter in the peroxo-oxalate process is the amount of hydrogen peroxide in solution. P.H. Duvigneaud *et al.* report that for a similar system (in absence of oxalate) also based on homogeneous precipitation the amount of hydrogen peroxide needs to be very high (H_2O_2:Ba = 40:1) to ensure complete precipitation of all the barium [15]. We found that when the ratio hydrogen peroxide over barium is changed from 40:1 to 5:1, no change in the composition was found with XRF.
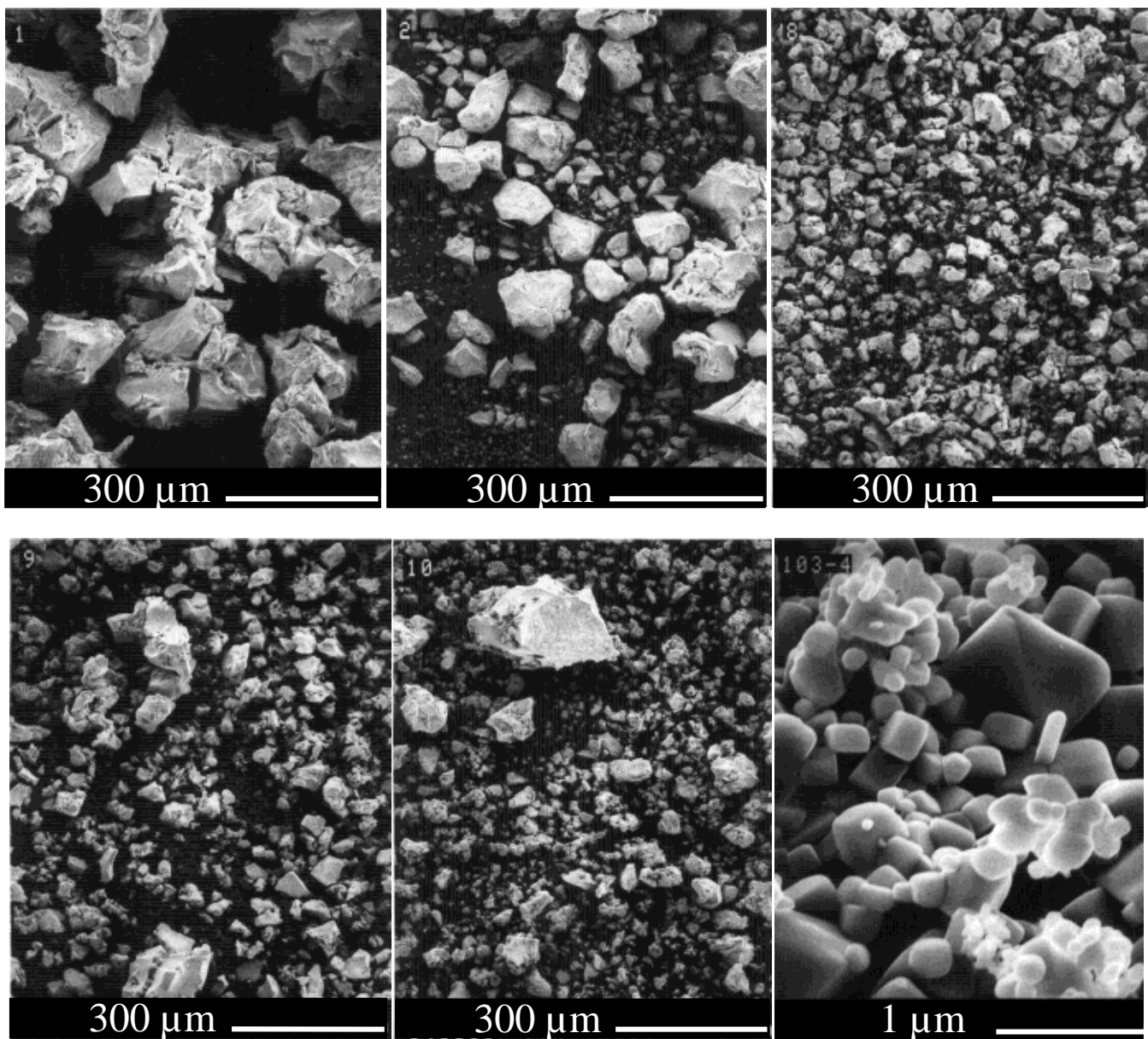
Figure 7:   *Micrographs of calcined powders prepared from a chloride precursor and at pH=9 using different precipitation temperatures. On top from left to right, 10, 20 and 40°C, below left 60 and middle 80°C. Below right detail of powder prepared at 60°C.*

When the precipitation temperature increases, the particle size of the dried-complexes and consequently in the calcined powders decreases. In *figure 7* this increase in particle size of the calcined powders can be observed. Powders prepared above 40°C consist of smaller aggregates than powders prepared below this temperature. This change in agglomerate size is probably due to the slow nucleation rate at lower temperatures. Because of this slow nucleation, more growth will take place at low temperatures. At high temperatures more nuclei are formed, and less growth takes place. Therefore at higher temperatures smaller particles are formed.

Another reason for the formation of large aggregates at a low precipitation temperature might be the larger amount of amorphous phase present at these low precipitation temperatures. The relation between the amount of amorphous phase and precipitation temperature is demonstrated in *figure 4*.

In *figure 8* the densification curve of a green body (chloride precursor, precipitated at 20°C) is shown. The sintering starts at a temperature of 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 *figure 9*. In this micrograph large grains are visible with an average grain size of 160 µm. The ceramic has a maximum dielectric constant at the Curie-temperature (88°C) of approximately 28.000, which corresponds to the required high value for this constant.

Due to the simultaneous presence of hydrogen peroxide and oxalate, the method as described in this chapter might also provide a basis for the preparation of barium titanate ceramics with different amounts of zirconium as well as barium titanate doped with other elements.
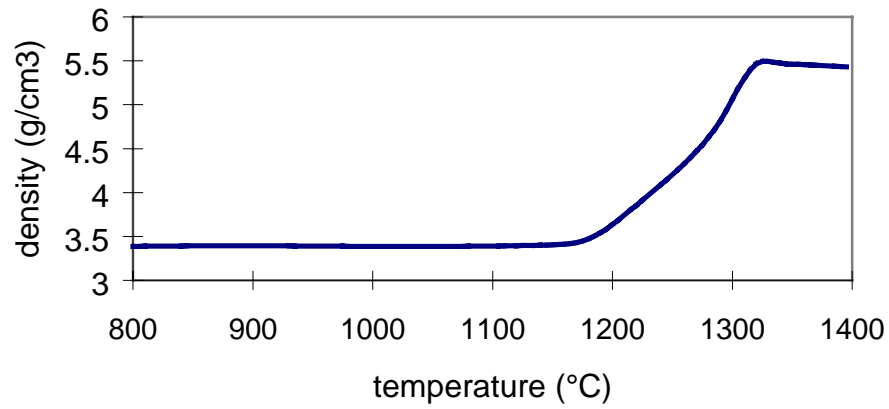
Figure 8:   Densification curve of a compact prepared from a chloride precursor at pH 9 and 20°C.
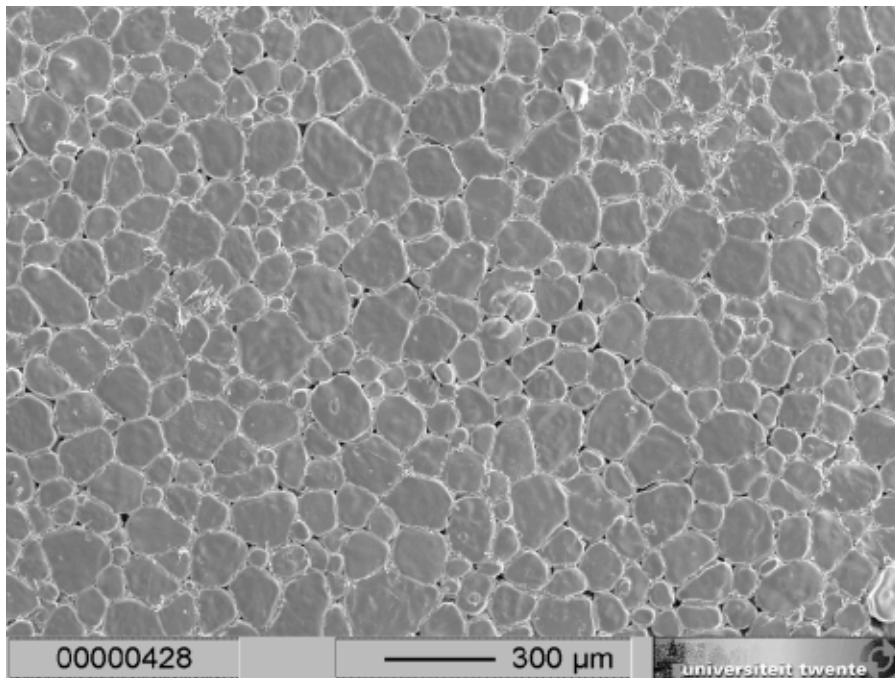

Figure 9:   Microstructure of a ceramic prepared with the peroxo-oxalate method.

4.4 Conclusions

For the peroxo-oxalate method as described in this chapter, 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 peroxo-oxalate process has to be conducted with chloride precursors at pH = 9. A precipitation temperature of 40°C is optimal, since at this temperature the lowest amount of second phase is formed .The precipitation temperature should not be too high, because at high temperatures condensation of precursors occurs. The pH during precipitation needs to be above 9, because only at high pH values a complex which precipitates stoichiometrically with barium is formed. The use of an alkoxide precursor has to be avoided because it will lead to second phase formation. The peroxo-oxalate method conducted at pH 9, 40°C and starting with a chloride precursor results in a stoichiometric, sinteractive powder of which the corresponding ceramic has a high dielectric constant at the Curie-temperature.

References

1. S. Iwaya, H. Masumura, Y. Midori, Y. Oikawa and H. Abe, "Non-linear polycrystalline barium titanate-type dielectric elements," *US patent* 4,404,209 (1983).
2. S.M. Neirman, "The Curie point temperature of $Ba(Ti_{1-x}Zr_x)O_3$ solid solutions," *J. Mater. Sci.*, **23** 3973-80 (1988).
3. D. Hennings and A. Schnell, "Diffuse ferroelectric phase transitions in $Ba(Ti_{1-y}Zr_y)O_3$ ceramics," *J. Am. Ceram. Soc.*, **65** [11] 539-44 (1982).
4. D. Hennings, "Barium titanate based ceramic materials for dielectric use," *Int. J. High. Tech.*, **3** 91-111 (1987).
5. R. McSweeney, K. Zuk and D. Williamson, "Square loop $Ba(Ti,Zr)O_3$ capacitors based on alkoxide derived $(Ti,Zr)O_2$ powders," in Proceedings of the First International Conference on Ceramic Powder Processing Science (Orlando Florida, November, 1987)
6. S. Kazaoui and J. Ravez, "Dielectric relaxation in $Ba(Ti_{0.8}Zr_{0.2})O_3$ ceramics," *J. Mater. Sci*, **28**, 1211-19 (1993).
7. P. Phule and S.H. Risbud, "Low-temperature synthesis and processing of electronic materials in the $BaO-TiO_2$ system," *J. Mater. Sci.*, **25**, 1169-83 (1990).
8. S. van der Gijp, A.J.A. Winnubst and H. Verweij, "An oxalate-peroxide complex used for the preparation of doped-barium titanate," Accepted for publication in *J. Chem. Mater.* (1998).

9.   A.I. Vogel, "Textbook of quantitative inorganic analysis," pp 319-40 4th ed. Revised by J. Bassett, R.C. Denney, G.H. Jeffery and J. Mendham (1978).

10.   J. Mühlebach, K. Müller and G. Schwarzenbach, "The peroxo complexes of titanium," *J. Inorg Chem.*, **9** [11] 2381-89 (1970).

11.   M. Stockenhuber, H. Mayer and J. Lercher, "Preparation of barium titanates from oxalates," *J. Am. Ceram. Soc., 76* [5] 1185-90 (1993).

12.   G. Busca, V. Buscaglia, M. Leoni and P. Nanni, "Solid-state and surface spectroscopic characterization of $BaTiO_3$ fine powders," *Chem. Mater.*, **6** 955-61 (1994).

13.   G.V. Jere and C.C. Patel, "The thermal stability of hydrated titanium peroxide and of some peroxy titanium compounds," *J. Inorg. Nucl. Chem.,* **20** 343-51 (1961).

14.   H.P.Abicht, D. Völzke, A. Röder, R. Schneider and J. Woltersdorf, "The influence of the milling liquid on the properties of powders and ceramics," *J. Mater. Chem*, **7** [3] 487-92 (1997).

15.   P.H. Duvigneaud, M. Gilbert and M. Promel, "Synthesis of n-doped barium titanate by precipitation from complexes," pp 77-81 in Euro-Ceramics 1, Proceedings of the First European Ceramic Society Conference (Maastricht, The Netherlands, June 1989) Edited by G. de With, R.A. Terpstra and R. Metselaar, London, UK, 1989.

5. Preparation of BaTiO$_3$ by homogeneous precipitation

Abstract

Three different methods are studied for the preparation of fine-grained BaTiO$_3$ powders by homogeneous precipitation:

1. Hydrolysis of barium and titanium alkoxide precursors, in which the required water is generated by an esterification reaction.

2. Precipitation of a barium-titanium complex as a result of thermal decomposition of Ba-EDTA.

3. Precipitation of a barium and titanium complex by the increase of pH caused by the hydrolysis of urea.

The properties of powders, prepared via these methods, and their sintering behaviour are as follows:

1. The esterification method results in a powder with a medium average aggregate size of about 3 µm and a sintered density of 90% which is higher than the value obtained with the other precipitation methods. The considerable differences, in hydrolysis rate between the barium and titanium precursors used, lead to second phase formation.

2. The complexation method gives the most promising results; 1 µm sized spherical aggregates were obtained which consist of smaller particles. The obtained sintered densities were up to 88%. The method can be optimised further to obtain values in excess of 95%.

3. The urea method results in large irregular aggregates and is therefore unsuitable for the preparation of BaTiO$_3$ ceramics.

5.1 Introduction

The crystal lattice of $BaTiO_3$ is based on the ideal perovskite structure and has small distortions leading to its interesting ferroelectric properties. Ceramics made from $BaTiO_3$ powders with specific dopants[*] have high dielectric constants, which strongly depend on grain size and hence on the microstructure [1]. Several preparation routes are described in literature for the production of (doped) barium titanate powders [2]. A distinction is made between mixed oxide and wet-chemical preparation processes. Mixed oxide processes contain less processing steps but generally result in less homogeneous powders and hence ceramics with a more irregular microstructure. If a more homogeneous, fine-grained ceramic microstructure and hence a better control of the powder morphology is required, the utilisation of wet-chemical powder preparation processes comes into scope. Most wet-chemical processes are based on precipitation of some precursor compound or mixture followed by calcination to obtain the proper $BaTiO_3$ phase. In this chapter there is distinguished between:

- *Heterogeneous precipitation* in which two different reactant solutions are mixed in solution so that a macroscopically heterogeneous liquid state is present for some time.

- *Homogeneous precipitation* in which nucleation and precipitation starts in an initially homogeneous liquid, containing all the reactants and the liquid state remains homogeneous during reaction.

In heterogeneous precipitation, which is most common, a precursor solution containing metal ions is added to a second solution with e.g. special pH or vice versa [3]. Heterogeneous precipitation suffer from the following disadvantages:

- Even when the solution is stirred extremely vigorously. Considerable concentration gradients will be present in the solution for some time.

- Due to the required stirring action, there is a high collision frequency between the particles, which results in the formation of large aggregates [4]. The collision frequency can be reduced to some extent by using special stirring rods or very dilute systems [5].

---

[*] In the present chapter we ignore the dopants and may speak of $BaTiO_3$, even when dopants may be present.

The above-mentioned complications are not related to homogeneous precipitation processes. In such a process, a homogeneous solution is prepared containing all metal ions and reactants in such a way that no precipitation occurs initially. Here, the actual precipitation is the result of a chemical reaction that becomes effective after a certain incubation period. The extent of this reaction can be adjusted by e.g. controlling the solution temperature while gradients are avoided at the same time. In homogeneous precipitation, concentration gradients are prevented at all stages while the stirring speed can be reduced drastically to a level that particle sedimentation is just avoided and the solution temperature is kept homogeneous. In this chapter a comparative study of three homogeneous precipitation methods for the preparation of $BaTiO_3$ powder by means of homogeneous precipitation is presented. The quality of the calcined powders is evaluated by characterisation of particle morphology, average chemical composition as well as compaction and sintering behaviour. The actual investigated preparation methods are presented in the following sections.

5.1.1 Esterification method

In the esterification method, homogeneous precipitation is accomplished by the in situ formation of water. The reaction occurs at elevated temperatures in a solution containing an alcohol and a carboxylic acid [6]:

$$R'COOH + R''OH \xrightarrow{\Delta T} R'COOR'' + H_2O \tag{1}$$

According to Mazdiyasni et al. the water formed by reaction (1) reacts immediately with barium and titanium alkoxides to form $BaTiO_3$ [3]:

$$Ba(OR''')_2 + Ti(OR'''')_4 + 3H_2O \rightarrow BaTiO_3 + 2R'''OH + 4R''''OH \tag{2}$$
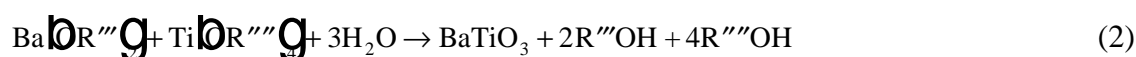
5.1.2 Complexation method

The complexation method is based on the thermal decomposition of a Ba-EDTA complex, which is dissolved in an aqueous solution. The Ba-EDTA complex decomposes above 40°C resulting in a gradual release of Ba^{2+} ions in the solution:

$$Ba(EDTA)^{2-} \xrightarrow{T>40°C} Ba^{2+} + EDTA^{4-} \tag{3}$$

The homogeneously released barium ions react directly with a titanium peroxo complex at pH = 9 to form an insoluble complex [7]:

$$Ba^{2+} + TiO_2(OH)_4^{2-} \xrightarrow{pH=9} BaTiO_2(OH)_4 \downarrow \tag{4}$$

The titanium peroxo complex is formed from titanium oxychloride and hydrogen peroxide at pH = 9, before decomposition is performed. The $BaTiO_2(OH)_4$ complex, formed by precipitation, is thermally converted to $BaTiO_3$ by calcination.

5.1.3   Urea method

The urea method is based on the pH-dependent structure of a titanium peroxo complex [8]. The general formula of this complex ion is $TiO_2(OH)_n^{n}$ in which n depends on the pH. Only when n = 6, which occurs at pH $\geq$ 9, a titanium species ($TiO_2(OH)_4^{2-}$) is present that reacts with barium to form an insoluble complex. The precipitation reaction in the urea method is also based on reaction (4). Contrary to what is the case in the complexation process, in the urea process the barium atoms are already present while the titanium peroxo complex is formed gradually by changing the pH from 3 to 9. This increase in pH is accomplished by the thermal decomposition of urea that starts above 60°C in an aqueous solution according to [9]:

$$(H_2N)_2CO + 3H_2O \xrightarrow{\Delta T} CO_2 + 2NH_4OH \tag{5}$$
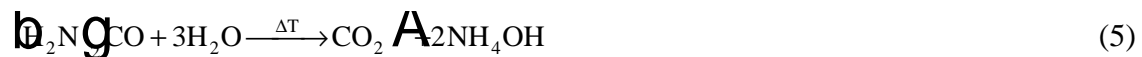
$BaTiO_3$ is finally obtained in the same way as in the complexation method namely by thermal decomposition of the complex.

5.2 Experimental

5.2.1   Esterification method

Barium isopropoxide was freshly prepared by adding an excess of Na-dried isopropanol (Merck, p.a.) to Ba metal (Merck) in a molar ratio of 30:1 under purified nitrogen. This mixture was refluxed until all the metal had reacted. The barium isopropoxide/isopropanol mixture was mixed with titanium isopropoxide (Aldrich 97%) and an excess of 2-methoxy ethanol (Merck p.a.) and acetic acid. This mixture was refluxed for two hours under a nitrogen atmosphere. The final reaction mixture had a composition, of [Ba]:[Ti]:[isopropanol]:[2-methoxy ethanol]:[acetic acid]=1:1:15:5:10 based on unreacted components. The solution was cooled to 0ºC and an excess of acetic acid (Merck p.a., 100%) was added slowly. The obtained solution obtained was refluxed for approximately 8 hours after which the precipitate was collected by filtration. The dried powder was calcined at 800ºC for 10 hours, using heating and cooling rates of 4ºC·min⁻¹. The calcined powder was ball-milled for 12 hours in 2-propanol.

5.2.2 Complexation method

A titanium peroxo complex was prepared by mixing Ti-isopropoxide (Aldrich 97%), H_2O_2 (30%, Merck, medical extra pure) and HCl (Merck, p.a., 37%). The pH of this solution was raised from 1 to 9 by adding ammonia, followed by the addition of a second solution, consisting of a mixture of $BaCl_2$ and EDTA (Merck p.a.). This sequence was chosen to avoid premature oxidation of EDTA by H_2O_2, which causes blocking of the nitrogen lone pairs and hence diminishes complexation strength. In the final mixture, however, the presence of H_2O_2 may have a favourable effect on the precipitation reaction because:

- The $TiO_2(EDTA)^{2-}$ complex is formed in equilibrium with $TiO_2(OH)_4^{2-}$ and $(EDTA)^{4-}$ and is decomposed by H_2O_2 [7].

- H_2O_2 may accelerate the breakdown of the $Ba(EDTA)^{2-}$ complex to form Ba^{2+}, which is necessary for reaction (4).

The composition of the reaction mixture, based on unreacted components was $[Ba]:[Ti]:[H_2O_2]:[EDTA]:[H_2O] = 1:1:10:2:11.000$. The barium concentration in the mixed solution was 10^{-2} M. The temperature of the solution in the reaction vessel was increased by heating on a hot plate at 50ºC for 5 hours or 2 l solution was placed in a microwaveoven at 350 W for 2 hours [4]. The precipitate was filtered and calcined at 700ºC for 10 hours, using a heating and cooling rate of 4ºC·min^{-1}.

5.2.3 Urea method

The barium titanate prepared by the urea method, was doped with a small amount of calcium and zirconium. It was expected that these additions did not affect the morphological properties of the obtained powder. Using the urea method, $BaCl_2$, $CaCl_2$, $ZrCl_4$ and $TiOCl_2$ (Merck p.a.) were dissolved in the appropriate ratio. Hydrogen peroxide was added together with a five fold excess compared to of urea (Merck p.a.). The final reaction mixture had a composition, based on unreacted components, of $[Ba+Ca]:[Ti+Zr]:[H_2O_2]:[urea]:[H_2O] = 1:1:10:5:16.000$. The solution was heated on a hot plate while vigorous stirring. The precipitation started at 80ºC and the mixture was kept for 3 hours on 100ºC. The precipitate was collected by filtration and washed and finally calcined at 900ºC for 10 hrs, using a heating and cooling rate of 4ºC·min^{-1}.

5.2.4 Characterisation

The decomposition of the washed filtrates that were dried at 120ºC overnight was followed by TGA (Stanton Redcraft STA 625). The TGA experiments were performed in normal air at atmospheric pressure; a flow rate of 20 ml/min (STP), a heating rate of $4°C \cdot min^{-1}$ and a temperature range of 25-1000°C were used. The morphology of the calcined powder and the microstructure of the sintered bodies were studied using Scanning Electron Microscopy (Jeol JSM 35CF). The crystallite size of the powder was investigated with Transmission Electron Microscopy (Philips EM30). BET-surface area measurements were performed on a Micromeretics ASAP 2400. X-Ray Diffraction (XRD) measurements were performed using Philips PW1710 equipment with Ni-filtered CuK_α radiation (λ=1.5408 Å). The chemical composition of the calcined powders was determined by X-Ray fluorescence (XRF) using a Philips PW 1480/10 X-ray spectrometer.

The volume distribution of the powder particles was measured by light scattering with a Microtrac X-100 (Leeds and Northrup). Samples were made by pre-treating approximately 15 mg powder in 40 ml water with ultrasonic energy (30 W) 3 times for 20 seconds with a Branson Sonifier 450. For the interpretation of the measurements it was assumed that the powder particles were reflecting light and were spherical.

Ceramic discs with a diameter of 15 mm and a thickness of 5 mm were obtained by pre-pressing the powder uniaxially at 80 MPa and subsequently isostatic pressing at 400 MPa. All compacts were sintered at 1300°C for 10 hours in an oxygen atmosphere using a heating rate of $2°C \cdot min^{-1}$ and a cooling rate of $4°C \cdot min^{-1}$. Non-isothermal densification was studied with a Netzsch 410 dilatometer. Density measurements were performed by the Archimedes technique using mercury. The relative density was based on a theoretical $BaTiO_3$ density of $6.02 \ g \cdot cm^{-3}$. The microstructure of polished samples was revealed by thermal etching at a temperature, 10°C below the sintering temperature.

5.3   Results and discussion

5.3.1   Esterification method

Addition of acetic acid to the aqueous solution, containing titanium and barium, results initially in the formation of a small amount of white precipitate, caused by traces of water in the acetic acid. Because of the low pH the precipitate redissolves after a few minutes and the actual precipitate starts to form after approximately 30 minutes of heating the clear precursor solution. The TGA results for the dried precipitate depicted in *figure 1* show significant weight losses at temperatures, just above 300°C and 700°C. The weight loss below 350ºC is due to loss of water and the decomposition of organic derivatives. At 350°C $Ba_2Ti_2O_5CO_3$ is formed from $BaCO_3$ which is in turn a product of the reaction between Ba^{2+} and the organic constituents. $Ba_2Ti_2O_5CO_3$ is stable up to 700ºC [10]. The TGA results are not consistent with a zero weight loss according to reaction (2) and neither are they with the continuous weight loss of 10% up to 900°C as found by Mazdiyasni et al. [3]. The latter is likely to be due to a continuous loss of absorbed water, CO_2 and remaining solvent. This implies that the precipitation mechanism in our case is different from the mechanism described by Mazdiyasni et al. [3]. The rather high weight loss observed at 350ºC may be ascribed to the possible ex-
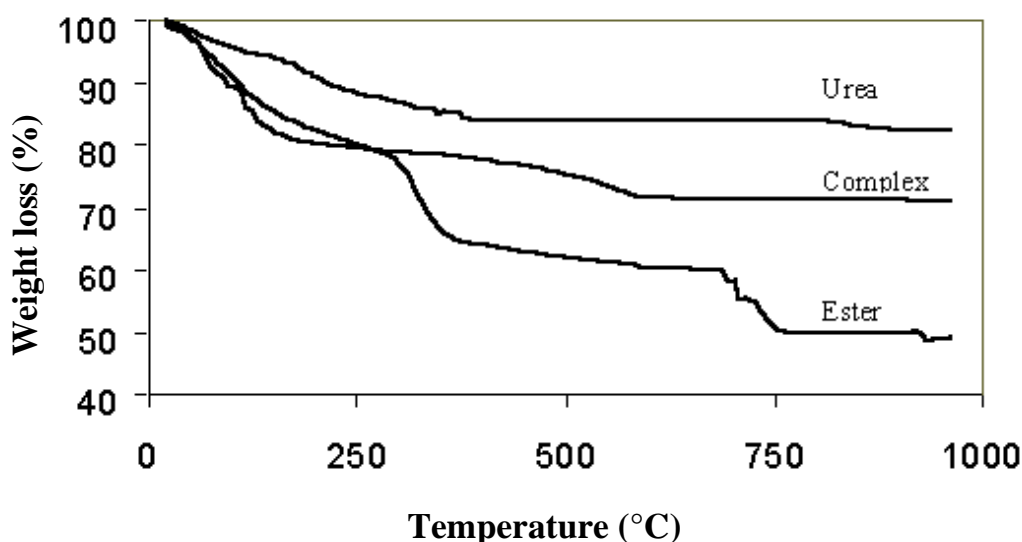

Figure 1:   *TGA results of dried precipitates prepared by esterification, complexation and the urea method.*

change of acetate ions with the isopropyl groups of the alkoxides [6]. This exchange is likely to result in the formation of the organic fragments in the precipitate as mentioned above earlier.

XRD results of the calcined powders are presented in *figure 2* in which it can be seen

Table 1: XRF results of the calcined powders.

Source	[Ba]:[Ti]
Esterification method	0.79
Complexation method	0.87
Urea method	0.15
Theoretical	1.0

that the esterification method results in the formation of cubic barium titanate with a small amount of $BaTi_2O_5$ second phase. Thus a small titanium excess is present in the precipitate which is confirmed by XRF measurements, see *table 1*. The titanium excess is probably caused by differences in hydrolysis kinetics of the single titanium and barium precursors. The reactant combination barium isopropoxide, titanium isopropoxide, isopropanol and 2-methoxy ethanol lead to the best results to obtain a 1:1 Ba:Ti ratio. This can be explained by an exchange reaction which takes place according to:

$$Ti(OR)_4 + 4CH_3O[CH_2]_2OH \rightarrow$$

$$Ti(OR)_{4-n}([CH_2]_2OCH_3)_n + nHOR + (4-n)CH_3O[CH_2]_2OH \qquad (6)$$
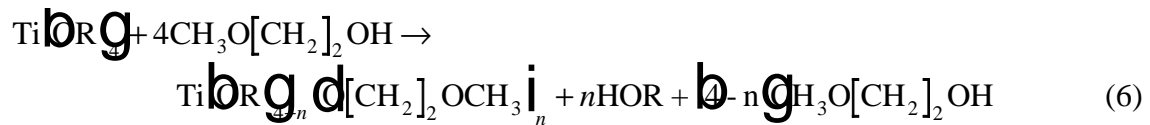
Because 2-methoxy ethanol is more acidic than water, fast hydrolysis of titanium is avoided when water is added to the mixture. This should allow the proper polycondensation reaction to take place and hence the formation of a gel with a barium over titanium ratio of 1 without precipitation of $Ti(OH)_4$ [11]. Several other combinations of alcohol and carboxylic acid (e.g. 2-propanol and formic acid) were tested to address the problem of Ti-stoichiometry control. It was found, however, that the combination of 2-methoxy ethanol and acetic acid results in a ratio closest to Ba:Ti = 1:1, the lowest amount of second phase and the highest sintered density. Interpretation of the results is complicated, however, due to the occurrence of the acetate exchange, since this exchange may reduce the hydrolysis rate as well [6]. Hence the explanation for the titanium excess in the precipitate can only be speculative at this stage:
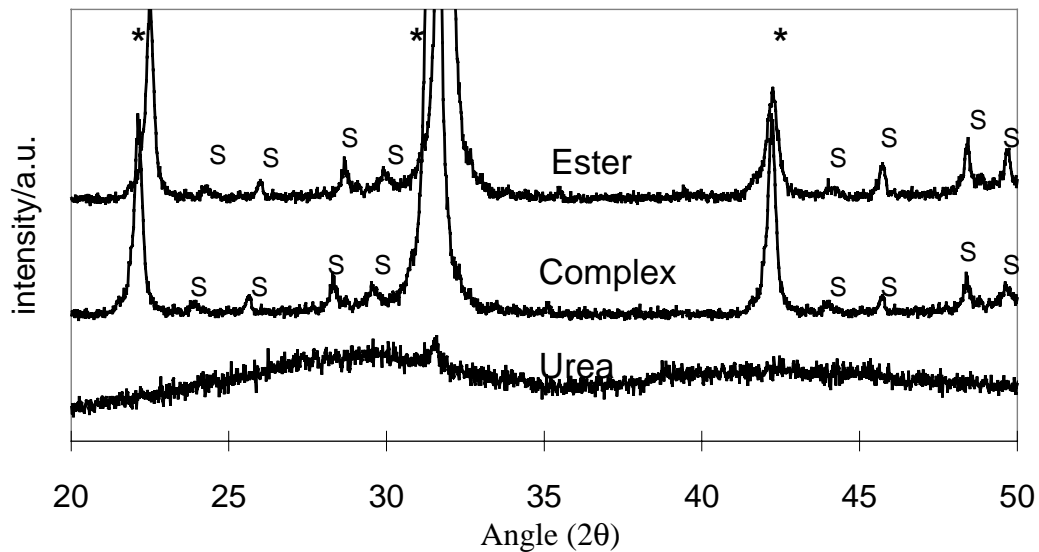
Figure 2: XRD of the calcined powders. Cubic perovskite is marked with (*); second phases, $BaCO_3$ and $BaTi_2O_5$ with s.

- The ligand exchange mechanism may occur for barium too because barium is more electronegative and therefore the exchange may be more efficient than for titanium. In turn, this may lower the hydrolysis rate of the barium compound to below that of the titanium compound.

- Barium hydroxide is well soluble in water, particularly at higher temperatures. Since the composition of the reaction mixture is such that a considerable excess amount of water can be formed, the liquid phase may contain a significant residual concentration of dissolved barium after precipitation. This barium is removed in the filtration step.

The latter explanation seems more reasonable. The particle size distribution of the calcined powder, determined by light scattering, is very broad: 50 vol% of the particles has a size below 2.9 μm and 90 vol% of the particles has a size below 10.2 μm. A SEM picture of the powder show that the particles have a porous internal structure is shown in *figure 3*. SEM recordings

Table 2: Green and final densities of the compacts.

Method	Green density (%)	Final density (%)
Esterification	51	90
Complexation	53	88
Urea	58	65

at lower magnification showed aggregates with sizes, comparable to values obtained by light scattering. By means of TEM (*figure 4*) it was established that the aggregates consist of crystallites with a size of approximately 0.07 µm. This size was confirmed by XRD line-broadening and BET measurements.

During sintering, densification of the green body starts at approximately 1150ºC, after which the relative density increases rapidly. The maximum densification rate is reached at 1215ºC and the final density is 90% (see *table 2*). The microstructure of the sintered compact is given in *figure 5* and reveals the occurrence of anomalous grain growth. This can be explained by the presence of titanium-rich phases in the powder; these
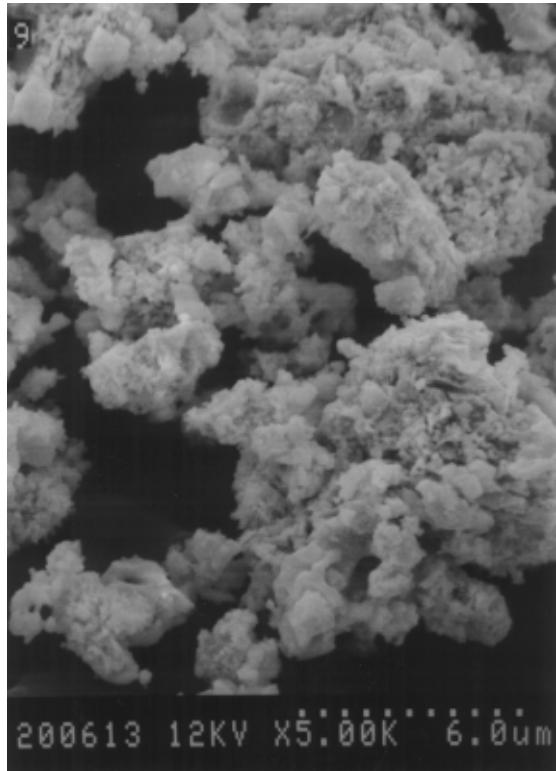
Figure 3: SEM micrograph of the calcined powder prepared by the esterification method; magnification 5000×.
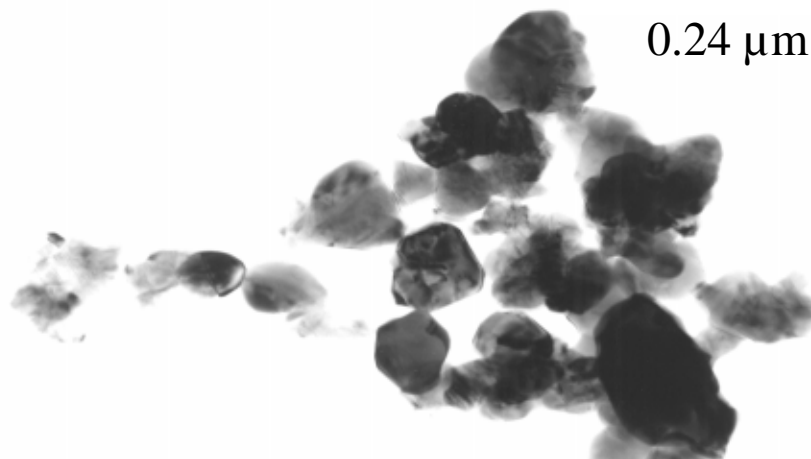

Figure 4:   TEM micrograph of powder prepared by the esterification method; magnification 94.000×.

phases form, an eutectic melt at 1312ºC together with BaTiO$_3$ [12,13].

5.3.2 Complexation method

After complete mixing, the barium-EDTA solution with the peroxo-oxalate solution, a clear yellow/green solution is obtained from which a yellow solid precipitate is formed upon heating. The yellow colour is characteristic for BaTiO$_2$(OH)$_4$ formed according to reaction (4). The TGA results for the dried precipitate in *figure 1* show weight losses at two different temperatures. Below 200ºC physically bound water is removed, whereas at approximately 550ºC the peroxide groups decompose. XRD analysis of the calcined powder showed the cubic barium titanate phase, with a small amount of second phase (BaTi$_2$O$_5$). The excess of titanium was confirmed by XRF measurements of which the results are presented in *table 1*. The composition of the powders was independent of the heating method (hot plate or microwave). The origin of the titanium excess may be found in an incomplete decomposition of the Ba-EDTA complex so that a small amount of titanium and barium remain in solution. The unreacted TiO$_2$(OH)$_2$ conden-
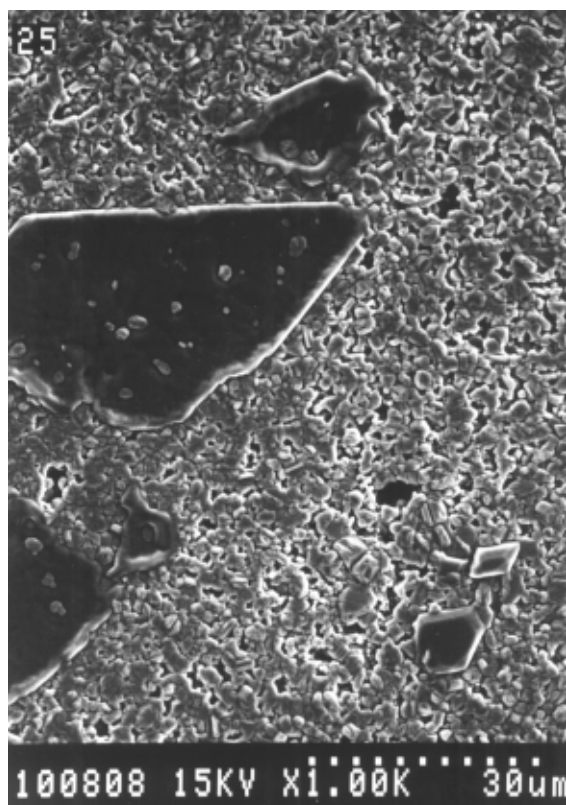

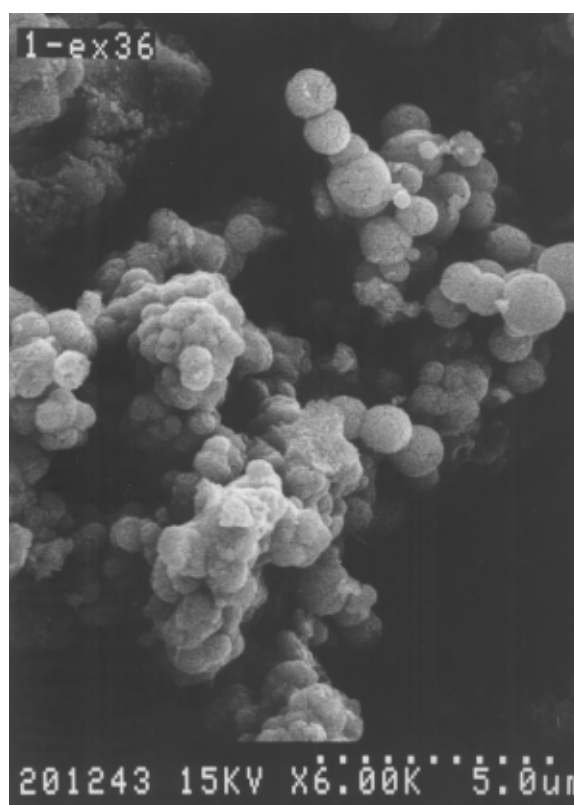| Figure 5 | Microstructure of thermally etched ceramic prepared with the esterification method. |

| Figure 6: | SEM micrograph of powder prepared with the complexation method. |

sates then slowly to a large insoluble titanium-hydroxide complex that is taken up in the precipitate while the barium remains in solution [8].

In *figure 6* a SEM micrograph of the calcined powder, prepared by heating on a hot plate is depicted. Spherical aggregates with a diamater of about 1 µm are visible. This size is in accordance with the same as the one determined by light scattering. Some neck formation between the aggregates is visible as well. The morphology of powders prepared by microwave heating is similar to those prepared by hot plate heating. Hence in this case, the size of the aggregates does not depend significantly on the extent of interparticle collision during stirring. The aggregation process is more likely to occur due to the intimate interparticle contact during the filtration step and the relatively long heating time for calcination. It was also found that the aggregate size of powders prepared by heating in a microwave oven does depend on the capacity of the microwave oven and therefore on the heating rate. Particle size measurements, performed directly after a temperature of 90°C was reached, showed that applying a microwave powder of 350 W resulted in an aggregate size of 2.2 µm, whereas increasing the powder to 1000 W gave grains of 4.6 µm (see *table 3*).

The excess of titanium and possibly the presence of remaining chloride ions lead to exaggerated grain growth during sintering. During sintering the relative density of the

Table 3:   *Effect of microwave power on heating rate and particle size.*

Power capacity (W)	Heating rate (°C/min)	D_{50} (µm)
160	3.75	*
350	7.25	2.2
500	10	2.7
650	12.75	4.6
750	15	3.9
1000	16.75	4.6

* No particles were formed at this power setting.

sample increased from 53 to 88%. The relatively low sintered density might be the result of the formation of larger cohesive agglomerates by neck formation (see *figure 6*).

5.3.3 Urea method

After addition of the hydrogen peroxide to the barium/titanium solution the solution is clear and red in colour. Upon refluxing of this solution an orange suspension is formed. The pH remains constant at 1 during refluxing. The formation of the suspension is accompanied by the release of small CO_2 gas bubbles, which is a reaction product of the hydrolysis of urea, see reaction (5). The TGA result of the dried precipitate in *figure 1* shows three different weight loss steps. Below 100ºC free water is removed and below 400ºC crystal water is removed. The third weight loss at 800ºC could be attributed by the conversion of $BaCO_3$ to BaO and, at the same time, of the titanium peroxo complex to TiO_2 [14].

The precipitate was calcined at 900ºC in air which resulted in the formation of an amorphous phase (see *figure 2*). As is shown in *table 1*, the powder produced with the urea method mainly consists of titanium oxide. This implies that the expected formation of the insoluble barium titanium peroxo species ($BaTiO_2(OH)_4$) did not take place. This may be caused by the fact that during decomposition of urea, the pH remains well below 7 so that the titanium peroxo complex will not or only partially be transformed into the $TiO_2(OH)_2^{2-}$ ions. As stated before, the latter complex represents the only complex-form for Ti^{4+} that is able to react with Ba^{2+} for the formation of an insoluble complex according to reaction (4). From a similar procedure for the precipitation of zirconia in the presence of chloride and nitrate ions, it is known that the pH finally reaches a value of 7-8, but only after heating for more than 5 hours [15]. In that case, most of the released hydroxyl ions have reacted with zirconium to form a homologous series of $[Zr(OH)_n]_{4-n}$ complexes. The large titanium excess indicates that, in spite of the presence of hydrogen peroxide, the precipitation mechanism for titanium is similar to the one developed for zirconium. This mechanism presumably leads to the formation of a homologous series of species with the general formula $\left(Ti_2O_5(OH)_m\right)^{2-2m}$ that reacts further to $TiO_3 \cdot xH_2O$ species (with $x \geq 1$, amount of hydrated water molecules) [8].

The urea method results in a low-density powder with an aggregate size of approximately 3 µm. The sintering experiments with powders prepared using the urea method

lead to ill-defined porous products which largely deviate from the perovskite stoichiometry and are therefore not interesting.

5.4   Conclusions

The preparation of $BaTiO_3$ powders by different homogeneous precipitation techniques, results in powders with different morphologies (see *figures 3 and 6*). Regardless of morphology, none of the three preparation methods can yet be applied because the final chemical composition of the powders cannot be kept sufficiently under control. The esterification method results in powders with the smallest aggregate size. The mechanism of precipitate formation in this process is not clear, but is obviously different from the one proposed by Mazdiyasni et al.[3]. An important complication in the esterification method is the fact that water, released in the reaction between isopropanol and acetic acid, reacts differently with single titanium and with barium precursor compounds. This easily results in the formation of a small amount of second phase in the final ceramic. In addition, the hydrolysis reaction may be unpredictably affected by the occurrence of exchange reactions between precursor ligands and ester forming reactants. Possible improvements with the esterification method might be obtained if:

- A single precursor molecule is used, containing all metal ions in the proper ratio.

- The exchange reactions with the precursor can be sufficiently suppressed. This can possibly be accomplished by using bulky acid molecules for which the exchange reactions are sterically hindered.

In the urea method, the pH is too low for the formation of a titanium compound which can react with barium. The powder prepared by this method, consequently, contains a very large titanium excess so that it is unlikely that the urea method, or any other similar method with controlled release of OH^- ions, will be suitable for the preparation of a high-quality barium titanate powder.

Despite the second phase formation and the fact that the sintered compact has a bit lower density than the compact formed by the esterification method, the complexation method seems most suitable to prepare uniform spherical aggregates. The titanium excess in the powder prepared by the esterification method results in the formation of a liquid phase during sintering. This liquid phase led to excessive grain growth accompanied by considerable pore entrapment hampering full densification. The sintering be-

haviour of the powder obtained with the complexation method can be improved further if:

- Neck formation between aggregates can be avoided by surface-chemical means or by a deagglomeration treatment afterwards.

- The titanium excess can be avoided by the application of a less reactive precursor or titanium complexation so that a more balanced precipitation is obtained.

To further develop a suitable route for the homogeneous precipitation of BaTiO$_3$ powders in a systematic way, more detailed insight is required in the chemistry of the complete hydrolysis and condensation mechanism, including ligand exchange reactions. The use of emulsion techniques or self-organising systems in the liquid phase, for instance, may lead to further improvements in powder composition and particle morphology.

In this chapter all syntheses were performed in batch reactors in which the reaction conditions at the beginning and at the end of the precipitation are not entirely the same; this may influence the product properties. If, for instance, the ionic strength of the solution changes during the batch reaction, this may affect particle/aggregate size in the final product due to changes in colloid chemistry [4]. Hence it is expected that significant improvements in composition control and powder morphology could be achieved if the precipitation would be performed in a continuous mode.

Acknowledgements

References

1. G. Arlt, D. Hennings and G. de With, "Dielectric properties of fine grained barium titanate ceramics," *J. Appl. Phys*. **58** (1985) 1619-25.
2. P.P. Phule and S.H. Risbud, "Review: Low temperature synthesis and processing of electronic materials in the BaO-TiO$_2$ system," *J. Mater. Sci.* **25** (1990) 1169-83.
3. K.S. Mazdiyasni, R.T. Dolloff and J.S. Smith II, "Preparation of high-purity submicron barium titanate powders*," J. Am. Ceram. Soc*., **52** [10] (1969) 523-26.
4. Y.T. Moon, D.K. Kim and C.H. Kim, "Preparation of monodisperse ZrO$_2$ by the microwave heating of zirconyl chloride solutions," *J. Am. Ceram. Soc.,* **78** [4] (1995) 1103-1106.
5. A. Mersmann, Crystallisation handbook, 1995 New York.

6. I. Laaziz, A. Larbot, C. Guizard, A. Julbe and L. Cot, "Hydrolysis of zirconium propoxide by an esterification reaction," pp 71-76 in *Better ceramics through chemistry V*. Proceedings of the Materials Research Society Symposium (San Fransisco, CA, April 1992). Edited by M.J. Hampden-Smith, W.G. Klemperer and C.J. Brinker. Materials Research Society, Pittsburgh, PA (1992).

7. P. Gheradi and E. Matijevic, "Homogeneous precipitation of spherical colloidal barium titanate particles," *Coll. Surf.*, **32** (1988) 257-74.

8. J. Mühlebach, K. Müller and G. Schwarzenbach, "The peroxo complexes of titanium," *J. Inorg Chem.*, **9** [11] (1970) 2381-89.

9. J.J. Geus, "Production and thermal pretreatment of supported catalyst", pp 1-33 in *Preparation of catalyst III*. Edited by G. Poncelet and P.A. Jacobs, Elsevier, Amsterdam (1983).

10. D. Hennings, G. Rosenstein and H. Schreinemacher, "Hydrothermal preparation of barium titanate from barium-titanium acetate gel precursors," *J. Eur. Ceram. Soc.*, **8** (1991) 107-15.

11. G. Lemoine, B. Gilbert, B. Michaux, J.P. Pirard and A.J. Lecloux, "Synthesis of barium titanate by the sol-gel process," *J. Non Cryst. solids*, **175** (1994) 1-13.

12. H.M. O'Bryan, Jr., and J. Thomson, Jr., "Phase equilibria in the TiO₂-rich region of the system BaO-TiO₂," *J. Am. Ceram. Soc.*, **57** [12] (1974) 522-26.

13. D.F.K. Hennings, R. Janssen and P.J.L. Reynen, "Control of liquid-phase-enhanced discontinuous grain growth in barium titanate", *J. Am. Ceram. Soc.*, **70** [1] (1987) 3-27.

14. P.H. Duvigneaud, M. Gilbert and M. Promel, "Synthesis of n-doped barium titanate by precipitation from complexes," pp 77-81 in: Euro-Ceramics 1, Proc. First European Ceramic Society Conf. (Maastricht, The Netherlands, June 1989) Edited by G. de With, R.A. Terpstra and R. Metselaar, London, UK, 1989.

15. J.L. Shi and J.H. Gao, "Preparation of spherical zirconium salt particles by homogeneous precipitation," *J. Mater. Sci.*, **30** (1995) 793-99.

6. *Chemical homogeneity of several Zr-doped barium titanate ceramics*

Abstract

In zirconium-doped barium titanate ceramics, chemical homogeneity can be related to the maximum value of the dielectric constant at the Curie temperature. To study the homogeneity effect several techniques (XRD, SEM/TEM-EDX, EPMA and auger) for the determination of homogeneity are discussed and compared. Three different powders were considered, a wet-chemical prepared powder, a commercial hydrothermal prepared powder and a powder prepared by a mixed oxide process. Ceramics were sintered at a high sintering temperature for a long prolonged time. Due to diffusion at the sintering temperature of 1400°C the difference in homogeneity between the three ceramics is difficult to determine. Auger spectroscopy seems to be the most useful technique to determine these minor differences in the pulse-generating ceramic.

6.1   Introduction

Doped barium titanate can be applied as pulse-generating device in discharge capacitors used in lamp starters [1]. For this application non-linear dielectric behaviour is required. To obtain this non-linearity at room temperature, the material must possess a steep gradient in the polarisation versus electric field hysteresis curve. If the maximum value for the dielectric constant at the Curie-temperature is exceptionally high, this steep gradient and consequently the desired non-linearity are obtained automatically.

To achieve the required high value for the dielectric constant at the Curie-point temperature, two aspects are important:

- The phase transitions present in barium titanate, cubic-tetragonal, tetragonal-orthorhombic and orthorhombic-rhombohedric must overlap, which can be achieved by doping barium titanate with 10% zirconium [2,3]. In this manner a Curie temperature

of approximately 90°C is obtained. The zirconia must be distributed randomly over the material in such a way that the composition is the same throughout the ceramic body. Compositional fluctuations will lead to a spreading of phase transition temperatures and therefore to a lower value of the maximum dielectric constant [4,5]. In other words the material must be chemically homogeneous.

- The internal stress in the final ceramic must be as low as possible. Mechanical stress in the material gives rise to a lowering of the maximum value for the dielectric constant [6]. Internal stress is introduced during cooling after sintering, because in the case of zirconium-doped barium titanate, at the Curie-temperature the unit cell of the material changes from cubic to rhombohedric. The amount of stress can be reduced by the formations of domains. The volume fraction of domains becomes larger in large grains, this can be explained by a lower volume fraction of domains in the vicinity of grain boundaries. Therefore, to obtain high values for the dielectric constant at the Curie-temperature, the grains of the ceramic must be as large as possible. Consequently high sintering temperatures are required.

Hennings et al. claim that the mechanical stress in the material and not chemical homogeneity determines the height of the dielectric maximum [6]. On the other hand, other authors claim the existence of a relation between the chemical homogeneity and the height of the dielectric maximum. However, some authors do not provide data concerning the homogeneity [2,4]. While other authors only use XRD to study the differences in homogeneity between various sintered compacts [3].

In this chapter the homogeneity of zirconium-doped barium titanate powder and ceramics is studied in more detail. Homogeneity can be described by any criterion of inhomogeneity, which is defined as an intrinsic material property of the material, expressing a really existing deviation of at least one measuring result from a reference result [5].

Ceramics were prepared from three powders: a mixed oxide power, a commercially prepared hydrothermal powder[1] and a powder prepared according to the peroxo-oxalate

---

[1] Sakai chemical Industry Co., Ltd., Japan

method [7,8]. To find the most suitable characterisation technique for the determination of chemical homogeneity in doped barium titanate powders and derived ceramics, a number of different techniques are used: TEM-EDX, XRD, SEM-EDX, Auger and EPMA.

The choice of characterisation technique is directly related to the question on which scale the homogeneity measurements should be performed. Detection on an atomic scale is tedious, while it does not provide representative data for the whole sample. An important indication concerning the scale of homogeneity characterisation is the scale on which the dielectric behaviour is defined. Since the permittivity of barium titanate ceramics can be considered as the sum of the volume contribution and a domain wall contribution, it is more fruitful to look at the homogeneity on the domain size scale [9].

With the available characterisation techniques, differences in homogeneity between the three powders and their corresponding ceramics are studied.

6.2 Experimental

6.2.1 Powder preparation

Mixed oxide powders were prepared by mixing the appropriate amounts of ZrO_2, TiO_2 and $BaCO_3$ followed by ball-milling in isopropanol, drying and calcination for 5 hours at 1200°C. Both heating and cooling rates were 5°C·min^{-1}. After calcination the powders were deagglomerated in cylohexane, dried and finally ball-milled again in isopropanol.

The peroxo-oxalate method is based on the complexation of zirconium, titanium and barium with hydrogen peroxide and oxalic acid at pH 9 in an aqueous environment. The method is described in more detail elsewhere [7,8].

The hydrothermally-prepared powder was obtained from Sakai (Japan). To prevent irregular compaction the Sakai powder was ball-milled for three hours in isopropanol.

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

6.2.2 Characterisation

The chemical composition of the calcined powders was measured by X-Ray fluorescence (XRF) (Philips PW 1480/10). The morphology of the powders was studied by transmission

electron microcopy (Philips CM30 Twin/STEM) in combination with energy dispersive X-ray spectroscopy (EDX) (KEVEX) using X-ray spectroscopy the composition of small grains (e.g. small aggregates) within the powders was studied as well.

Non-isothermal densification was performed with a Netsch 410 dilatometer. These experiments were conducted with a heating rate of $2°C·min^{-1}$ and a cooling rate of $4°C·min^{-1}$, the holding time at the sinter temperature of 1400°C is 6 hours. Density measurements were performed with the Archimedes technique using mercury.

To study the concentration deviations in the powders and ceramics SEM-EDX measurements were performed with a field emission scanning electron microscope (FE-SEM, Hytachi, type S800; EDX (KEVEX)), the measurements were conducted randomly. However, no concentration measurements were performed in pores or at grain boundaries. To measure the concentration in ceramics, Auger measurements were performed in an area
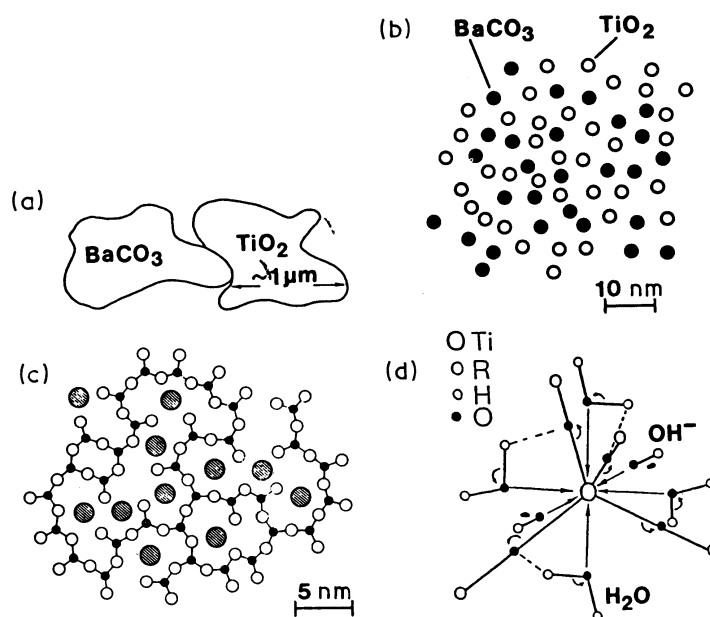

Figure 1: Schematic overview of the mixing states for different preparation methods: (a) Mixed oxide; (b) precipitation; (c) complexation; (d) sol-gel; (e) cubic perovskite lattice, Copied from Phule [10].

of 50 by 60 µm. In this area 20 points were taken on fixed locations. The measurements were conducted with a Scanning Auger Multiprobe (PHI-600 SAM) The following peaks were measured: Zr1(ke:147eV; ZrMNN), Ti1(ke:387eV;TiLMM), Ti2(ke:418eV;TiLMM) and Ba3(ke:584 eV;BaMNN). The spot size was 0.1 µm.

Electron probe microanalysis (EPMA) measurements were performed to measure the concentrations in the ceramics. The measurements were performed in the Gemeinschaftslabor für Electronenmikroskopie, RWTH Aachen, the measurement conditions were: 15 keV beam energy, 60 nA beam current, spot size 30 µm, the standards were barium titanate and pure zirconium. Again the location of the measurements were taken randomly over the sample, but no concentration measurements were performed in pores or at grain boundaries.

To study the homogeneity of ceramics, line broadening of a crushed ceramic sample was measured by XRD (Philips X'pert-1) on basis of the [2,2,0] peak. Philips (X'pert-) with-filtered Cu Kα1, λ=1.5408 Å.

6.3   Results and discussion

Due to the large scale of mixing the chemical homogeneity is expected to be lesser in mixed oxide prepared powders than in wet-chemical prepared powders, see *figure 1* [10]. It can be seen that the degree of mixing in mixed oxide powder is larger than the mixing in several wet-chemical techniques. Local differences in the mixed oxide powders are expected to occur due to the slow reaction and diffusion of the more refractory constituent ZrO_2 [4].

To reduce stress, the grains of the ceramics must be large. To promote grain growth next to high sintering temperatures and long sintering times, the occurrence of liquid phase sintering is needed. As a consequence of this high sintering temperature and long sintering
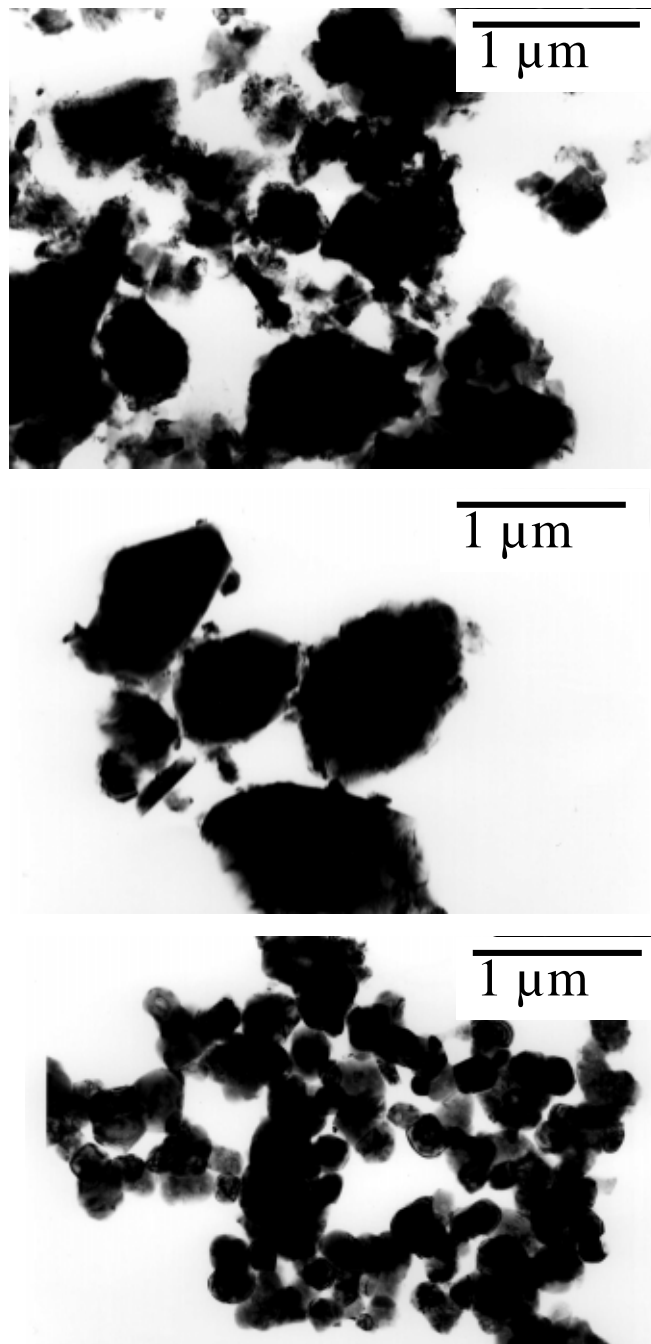
Figure 2:   TEM micrographs of calcined powders,   top = peroxo-oxalate powder,   middle = mixed   oxide powder and below = Sakai powder.
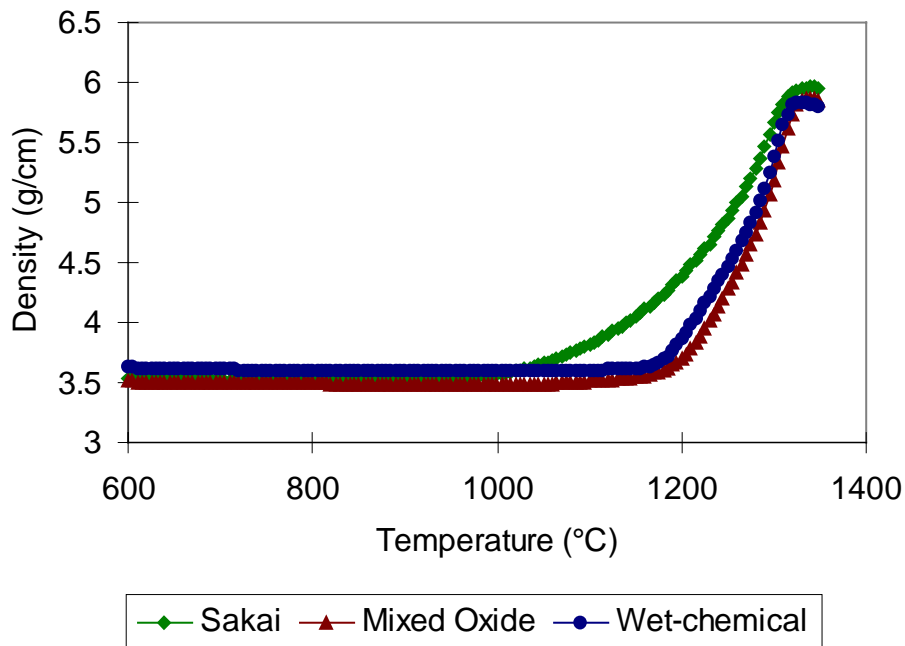
Figure 3:   *Densification curves of compacts prepared out of the three different powders.*

times diffusion is fast, which results in a homogeneous material. Even second phases may disappear as a result of this process [11].

6.3.1 Powder

Because in dense ceramics diffusion will take place more rapidly, it is important to know at what temperatures the ceramic becomes dense. Therefore, a comparison of the sinterability of the three powders is made. The composition of the powders is measured with XRF, see *table 1*.

The peroxo-oxalate powder contains somewhat less zirconium than the Sakai and the mixed oxide powder. The A/B ratio[2] is somewhat larger for the Sakai powder. All three powders consists of single-phase polycrystalline perovskite zirconium-doped barium titanate.

---

[2] A over B ratio; amount of barium over (titanium plus zirconium).

Table 1: *Composition of the powders as measured with XRF, measurement error 1%.*

Power	Ba	Ti	Zr	A/B
Sakai	1.000	0.913	0.100	1.012
Peroxo-oxalate	1.000	0.914	0.092	1.004
Mixed oxide	1.000	0.914	0.103	1.017

In *figure 2* TEM-photo's of the powders are shown. It is visible that the Sakai powder has an aggregate size of approximately 0.2 µm and that it is agglomerated to larger units. Powders produced with the mixed oxide method (0.3-1 µm) and the peroxo-oxalate method (0.1-0.8 µm) have a large average aggregate size and a broader size distribution. The Sakai powder has the highest sinterability. A green compact prepared from the Sakai powder starts to densify at approximately 1050°C. The sinteractivity of a compact prepared from the peroxo-oxalate method and from a compact prepared by the mixed oxide method are similar, see *figure 3*. Both start to densify at approximately 1200°C. For all three powders the final density is obtained after sintering at temperatures higher than 1350°C. The final density of the ceramics prepared from the three powders is approximately the same and exceeds 95%.

6.3.1.1 XRD-line broadening

In *table 2* the results for the XRD line broadening as measured on the three different powders are given. Broadening may be the result of chemical inhomogeneity but also the result of internal stress in the material or small particle size. Since the particle size of the Sakai powder is the smallest, the broadening due to particle size is the largest for the Sakai powder. XRD line broadening is not suitable for the

Table 2: *Line broadening as measured with XRD on calcined powders.*

Sample ID	Peak width (° 2-theta)
Sakai	0.868
Mixed oxide	0.361
Peroxo-oxalate	0.439

determination of chemical homogeneity in powders because it is not possible to distinguish line broadening due to stress, particle size or homogeneity.

6.3.1.2 TEM-EDX

The use of EDX as a method for concentration analysis for zirconium-doped barium titanate is difficult because the Ba-L and Ti-K lines of the spectrum overlap. TEM-EDX provides more reliable data, because the Ba signal at 35kEV is isolated. The titanium signal, however, still suffers from overlap with the barium signal, so that quantitative concentration values found with TEM-EDX are not very reliable. However, when the same fitting procedure after measurement is repeated several times, the standard deviation found in these concentration values is a good measure of inhomogeneity.

In *table 3* the results of the standard deviation obtained for concentration measurements with TEM-EDX are shown. The concentration measurements were conducted on a small number of grains. The standard deviation with respect to the barium and titanium are comparable for the Sakai and the peroxo-oxalate powders. In case of the mixed oxide powder a somewhat larger standard deviation is found.

Table 3:   Standard deviation found for TEM-EDX.

Sample	Ba	*Ti*	*Zr*
Mixed oxide	*7*	10	30
Peroxo	9	9	20
Sakai	9	8	16

6.3.2   Ceramic

6.3.2.1 EPMA

Electron probe microanalysis (EPMA) is based on the spectrometry of characteristic X-rays emitted by elements under the effect of an incident electron beam. Unlike X-ray fluorescence, the primary beam can be focused on the specimen [12]. The spot size of the electron beam used in EPMA is large and comparable to the grain size. The EPMA measurements were conducted at random within an area of 500 by 500 µm.

The results of the electron probe microanalysis are given in *table 4*. Note that in case of a sample prepared according to the peroxo-oxalate process a titanium-rich second phase was detected, which is not taken into account in the calculation of the standard deviation of the concentration.

Table 4:   *Results of EPMA measurements, the values given for each element is the concentration deviation.*

Process	Number of meas.	Ba	Ti	Zr	O
Mixed	24	0.598	0.478	0.117	0.505
Peroxo	15	0.336	0.145	0.085	0.37
Sakai	25	0.283	0.153	0.039	0.261

The standard deviation obtained for the peroxo-oxalate and the mixed oxide prepared ceramics is larger than the deviation of concentration in the mixed oxide powder. The deviation of the zirconium concentration is in all three samples approximately the same. The high value found for the standard deviation in case of zirconium is due to the low zirconium concentration, which enlarges the measurement error. Hence the value found for zirconium is likely to be dominated by the experimental error of this technique.

6.3.2.2 SEM-EDX

SEM-EDX can be used as a concentration-characterisation technique for ceramics, because the surface of the ceramic sample is flat. Again, due to the overlap of the Ba-K and Ti-K lines no exact value for the concentration can be found. Also, for this characterisation technique it is found that if the same fitting procedure is used after each measurement, reliable information can be obtained about the standard deviation of the concentration in the ceramics. For SEM-EDX it was not possible to measure the isolated barium signal at

Table 5:   *Results of SEM-EDX measurements, the values given for each element are the concentration deviations Ceramics were sintered at 1450°C.*

Sample ID	Number of meas.	Ba	Ti	Zr
Sakai	20	3	3	18
Mixed	20	3	3	14
Peroxo	18	1	2	13

35 kEV, since the energy of the primary electron beam is less than this value. To measure this signal properly, the energy of the primary electron beam is required to be three to five times 35 keV.

The results of the SEM-EDX measurements are given in *table 5*. If more than 20 samples are measured, all sintered under different thermal conditions, resulting in different grain sizes etc., the deviation of the zirconium concentration obtained for in the hydrothermal prepared ceramic is a factor 1.6 larger than for ceramics prepared from of peroxo-oxalate and mixed oxide powders.

The standard deviation in the zirconium concentration is for this technique the largest too. The standard deviation in the barium and titanium concentration is comparable for each powder.

6.3.2.3 X-ray line broadening

In literature X-ray line broadening is the only technique that is described to give an indication about the chemical (in)homogeneity of ceramics [3]. However, characterisation of the homogeneity by means of X-ray line broadening has the disadvantage that

Table 6: *Line broadening as measured with XRD. Temperature profile is indicate as: e.g. A,B,C, A = sintering temp., B = heat. rate above 1250°C (below 1250° heat. rate is 2°C·min), C= dwell.; cool. rate 4°C·min^{-1}.*

Sample ID	Temperature treatment	Peak width (2θ)	Peak height (counts)
Sakai	1350,2	0.390	848
Sakai	1450,0.1	0.372	864
Mixed	1350,0.2	0.391	887
Mixed	1450,0.1	0.385	830
Wet	1400,2	0.415	620

information is gained over the bulk rather than information over selected spots.

Next to homogeneity, line broadening can also be caused by stress. To avoid this effect the ceramics are crushed before measurement, followed by thermal annealing to remove stress. The results of X-ray line broadening measurements are given in *table 6*. Little or no difference is visible between the values obtained for the three different ceramics. Approximately the same results were obtained by measurements of the [1,1,0] peak.

6.3.2.4 Auger

For electrical isolators like barium titanate, a lot of techniques that make use of charged parts suffer from charging. Charging is also present when Auger spectroscopy is used, which results in a possible shift of some peak positions [13]. To reduce the amount of charging, a low current

Table 7:   Standard deviations obtained with Auger for each element (%).

Sample ID	Number of points	Ba	Ti	Zr
Sakai	20	11	14	22
Peroxo oxalate	16	10	15	21
Mixed oxide	20	9	12	24

and high counting rates are used as well as an oxygen atmosphere, (approximately 3.10^{-6} Pa). [14]. The data presented in *table 7* are based on the peak-to-peak heights from the first derivative of the Auger spectrum, which is the most common method for (semi-) quantitative analysis after correction the intensity of each auger line with a sensitivity factor [13]. According to *table 7* the obtained standard deviations found for the three elements are approximately equal. The deviation for the zirconium concentration is larger than for the other elements, but the differences between the absolute deviation found with Auger spectroscopy is smaller than for the other measuring techniques. Note that the deviation for barium and zirconium is considerably larger than for the other characterisation techniques. This can be explained by the fact that the spot size for this technique is much smaller than for the other techniques. This has the consequence that a concentration value is obtained which correspondents to a small spot rather than a more averaged concentration value for a larger area, as is obtained with other techniques.

In *figure 4*, contour plots are given of the Auger measurements. In this figure the variation of the A over B ratio is given. For the Sakai sample one maximum (0.46) can be seen, the remainder of the analysis area has lower ratios. The same is valid for the mixed oxide sample, which has a maximum A/B ratio of 0.60. For the peroxo-oxalate sample the distribution in the ratio is more random. Note that only a small spot of the entire sample is measured.

Wet-chemical methods should result in a higher degree of mixing, see also *figure 1*. However, it is questionable whether the complete atomic mixing of the various elements is obtained or not. During calcination of the wet-chemically formed products in many cases a barium carbonate phase is formed often, which leads to small clusters of barium carbonate. On the other hand one should bear in mind that, after this demixing step, the diffusion paths for the formation of barium titanate are shorter than in case of the mixed oxide intermediates [10]. The different homogeneity characterisation techniques for ceramics show little or no difference is present between the three samples, which is confirmed by the relation between sintering temperature and broadening of the XRD signal as is given in *figure 5*. It can be seen that broadening of the XRD signal, which is the result of inhomogeneity, stress and/or crystallite size, decreases with increasing sintering temperature (see also chapter 7 for more details about this figure). The decrease of broadening at least indicates that high sintering temperatures lead to the homogenisation of the ceramic.
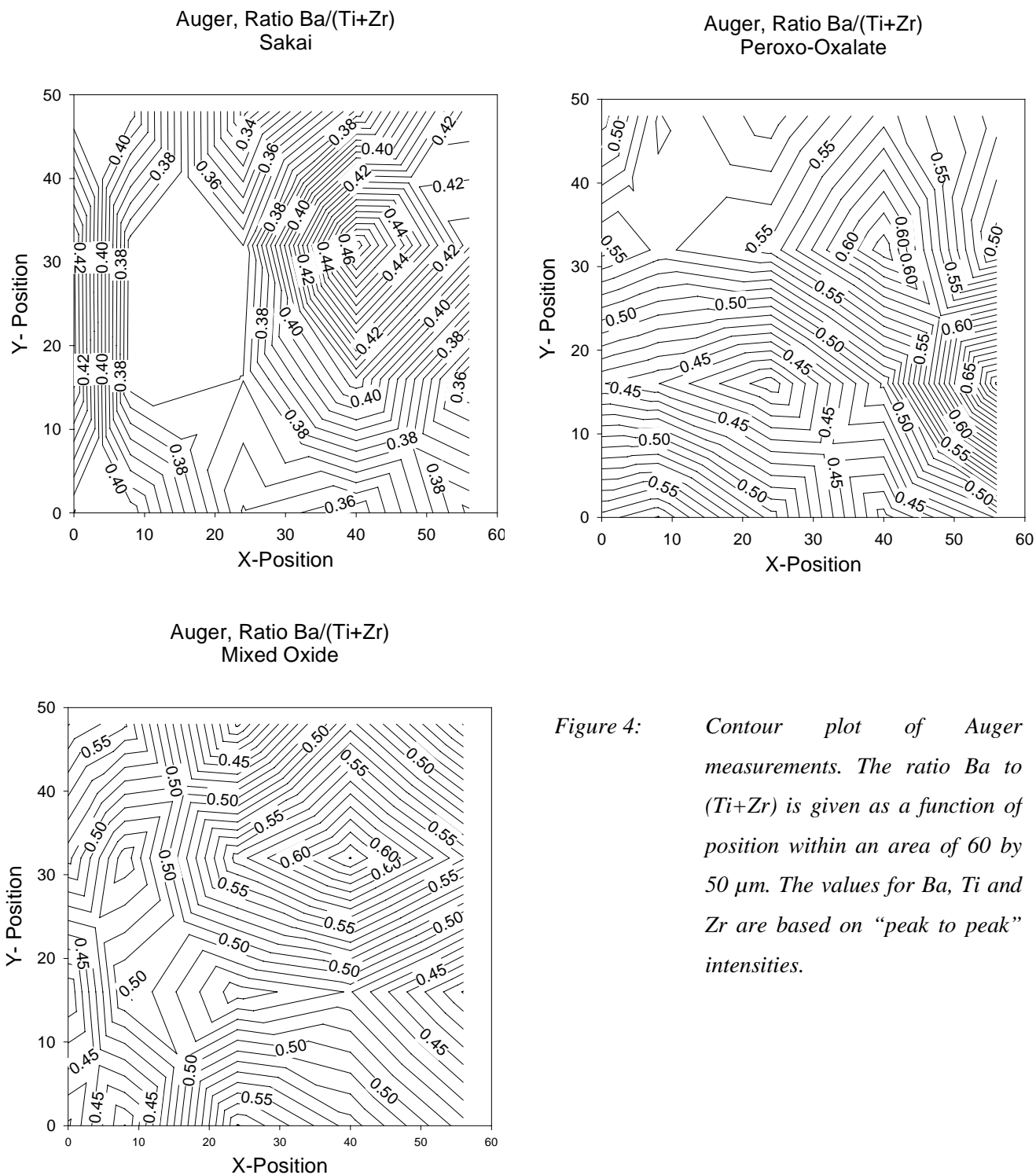
Auger, Ratio Ba/(Ti+Zr)
Sakai

Auger, Ratio Ba/(Ti+Zr)
Peroxo-Oxalate

Auger, Ratio Ba/(Ti+Zr)
Mixed Oxide

Figure 4:   *Contour plot of Auger measurements. The ratio Ba to (Ti+Zr) is given as a function of position within an area of 60 by 50 μm. The values for Ba, Ti and Zr are based on "peak to peak" intensities.*
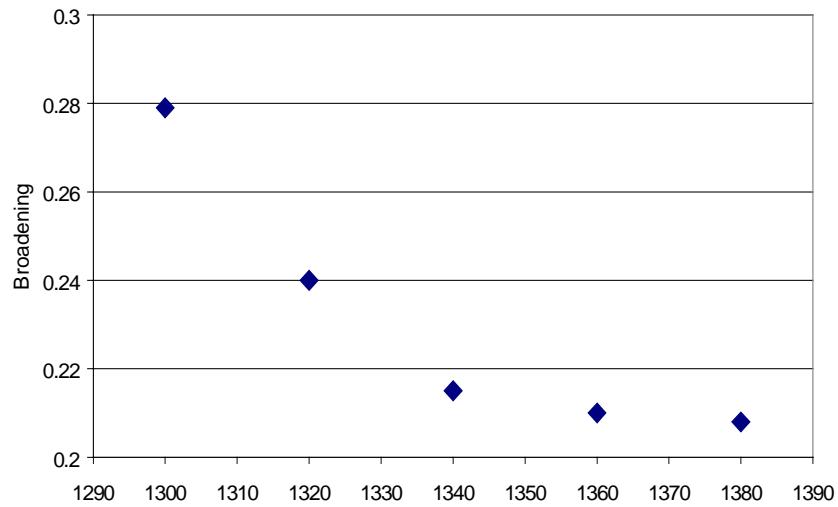
Figure 5:   *Broadening as measured with XRD as function of sintertemperature. XRD was measured on mixed oxide ceramics.*

6.4   General considerations

6.4   General considerations

The use of high sintering temperatures leads to uniform distribution of the additives through solid state diffusion. Therefore an inhomogeneous mixed oxide powder may still result in a homogeneous ceramic. Since wet-chemical processing is more difficult and requires the use of solvent, the question arises whether a wet-chemical method should be used for this type of application.

The improved morphology and homogeneity of the powder may attribute to a more homogeneous microstructure of the final ceramic and a reduction of the amount of porosity and finally contribute to higher grain growth.

6.5   Conclusions

The hydrothermally prepared Sakai powder is chemically homogeneous. However, due to diffusion during sintering little difference is observed between ceramics prepared from the Sakai powder, a peroxo-oxalate powder and a mixed oxide powder. SEM-EDX of the

ceramics even indicates a larger distribution for zirconium in case of the sample prepared from the Sakai powder.

Acknowledgements

References

1. M. Murata and A. Kitao, "Preparation of titanates," US patent 4,061,583. (1977).
2. R. McSweeney, K. Zuk and D. Williamson, "Square loop $Ba(Ti,Zr)O_3$ capacitors based on alkoxide derived $(Ti,Zr)O_2$ powders," in proceedings of the First international conference on ceramic powder processing science Orlando Florida, November, 1987.
3. S.M. Neirman, "The Curie point temperature of $Ba(Ti_{1-x}Zr_x)O_3$ solid solutions," *J. Mater. Sci.*, **23** 3973-80 (1988).
4. S. Kazaoui and J. Ravez, "Dielectric relaxation in $Ba(Ti_{0.8}Zr_{0.2})O_3$ ceramics," *J. Mater. Sci*, **28** 1211-19 (1993).
5. K. Uematsu, H. Tanaka, Z. Zhang and N. Uchida, *Ceram. Soc. Jpn.*, (1993) **101** 1400.
6. D. Hennings, "Barium titanate based ceramic materials for dielectric use," *Int. J. High. Tech. Ceram.*, **3** 91-111 (1987).
7. S. van der Gijp, A.J.A. Winnubst and H. Verweij, "An oxalate-peroxide complex used for the preparation of doped-barium titanate," *J. Chem. Mater.* **8** [5] 1251-54 (1998).
8. S. van der Gijp, A.J.A. Winnubst and H. Verweij, "Peroxo-oxalate preparation of doped-barium titanate," Accepted for publication in *J. Am. Ceram. Soc.*.
9. D. Hennings, Grain size and grain boundary effects in passive electronic components, Surface and near-surface chemistry of oxide materials ed. By J. Nowotny and L.C. Dufour, Elsevier science publishers, Amsterdam (1988) 479-505.
10. P. Phule and S.H. Risbud, "Low-temperature synthesis and processing of electronic materials in the $BaO-TiO_2$ system," *J. Mater. Sci.*, **25** 1169-83 (1990).
11. D. Hennings and G. Rosenstein, "Temperature-stable dielectrics based on chemically inhomogeneous $BaTiO_3$," *J. Am. Ceram. Soc.*, **67** [4] 249-254 (1984).
12. J.P. Eberhart, "Structural and chemical analysis of materials" pp 304-332.Wiley, Paris (1991).
13. A.J.A. Winnubst, "Electrical and interface properties of pure and modified yttria stabilized zirconia," PhD-Thesis, University of Twente (1984).
14. H. Gao, W. Maus-Friedrichs and V. Kemper, "Charging phenomena and charge compensation in AES on metal oxides and silica," *Surf. and Interf. Anal.*, **25** 390-96 (1997).

7. Microstructure and Dielectric Properties of BaTi$_{0.9}$Zr$_{0.1}$O$_3$

Abstract

In this chapter the dielectric properties of Zr-doped barium titanate are described. This material has an extreme high value for the permittivity at the Curie-temperature. The effect of mechanical stress and chemical homogeneity on the permittivity is studied. To prepare a ceramic which consists of grains with an average grain size above 300 µm a slow heating rate of e.g. $0.2°C \cdot min^{-1}$ is necessary. It is shown that stress has some influence on the maximum permittivity. No relation between the Curie-temperature or grain size and the maximum permittivity could be found, but both relations are related with stress. Sintering at 1500°C resulted in the highest value for the permittivity ($\varepsilon_r = 44526$) at the Curie-temperature, which is ascribed to the improved chemical homogeneity as a result of diffusion. Diffusion rules out differences in chemical homogeneity present in the calcined powders and green body before sintering.

7.1 Introduction

Doped or undoped barium titanate, is an often used component for electronic devices. One of the several possibilities is the use of zirconium-doped barium titanate, as a pulse generating device, which can be applied, amongst others, as a lamp starter in a discharge tube [1].

The height of the voltage peaks created by a non-linear device based on BaTi$_{0.9}$Zr$_{0.1}$O$_3$ depends on several parameters, but is first of all related to the height of the dielectric maximum at the Curie temperature [1]. An exceptionally high value for the permittivity maximum can be obtained when the phase transitions in barium titanate, from cubic to tetragonal to orthorhombic to rhombohedric, coincide [2,3]. This is achieved by doping barium titanate with 10% zirconium on the titanium site. The relative permittivity versus temperature behaviour for a BaTi$_{0.9}$Zr$_{0.1}$O$_3$ ceramic is given in *figure 1*.

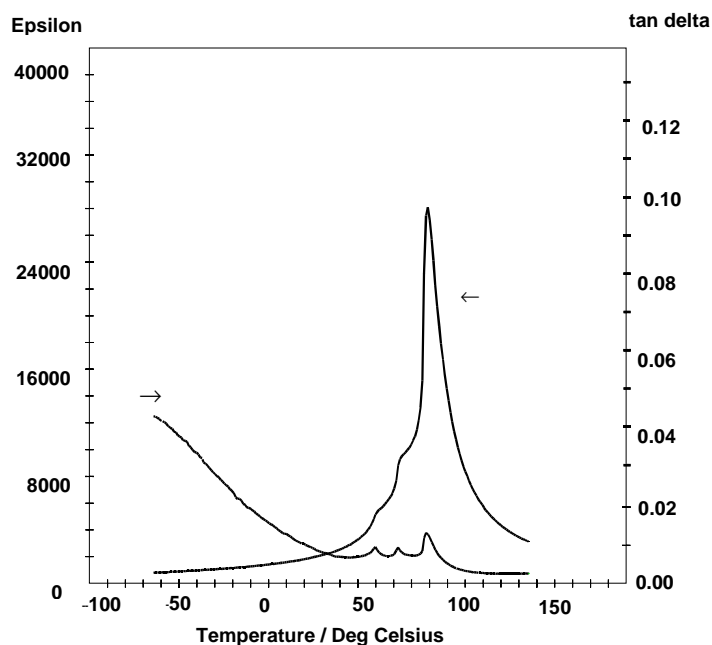In literature it is stated that the height of the maximum value for the dielectric constant

Figure 1:   *Relative permittivity versus temperature of BaTi$_{0.91}$Zr$_{0.09}$O$_3$ prepared by a mixed oxide process and sintered at 1500°C for 15 hours.*

can be influenced by two factors:

1. Chemical homogeneity [4-6]

2. Internal stress [2,3].

The effect of chemical homogeneity is explained by the fact that regions, which have a concentration other than the average concentration, have other phase transition temperatures with incomplete overlap of the different phase transitions. This results in broadening of the permittivity versus temperature curve and consequently lowering of the value of the maximum permittivity.

According to Hennings et al. chemical homogeneity is not the main reason for the distribution of Curie temperatures [2,3]. On basis of XRD profiles it was calculated that chemical homogeneity is only responsible for distribution over 4.5K while experimentally a broadening of approximately 28K was observed. Hence the occurrence of this broadening was assigned to internal mechanical stress [2,3]. Mechanical stress gives rise to the coexistence of ferroelectric and paraelectric phases. Stress is introduced during cooling after sintering as a consequence of a cubic to rhombohedric phase transition the Curie temperature [7]. Because only the ferroelectric phase has the required property for the pulse-generating devices, the presence of paraelectric phases lowers the height of the maximum permittivity. The amount of internal stress is largely reduced by domain formation, which in large grains is less restricted by the presence of grain boundaries. Consequently, the presence of large grains causes the formation of more domains in order to obtain less stress in the ceramic after cooling [3]. These large grains can be accomplished by using liquid phase sintering and a high sintering temperature.

In this chapter the effect of chemical homogeneity and internal stress on the dielectric properties of $BaTi_{0.9}Zr_{0.1}O_3$ is discussed in order to find out which effect is the most important. Ceramics prepared from powders with different scales of chemical homogeneity, are compared with respect to their dielectric properties and microstructure. The relation between the sintering conditions and the dielectric properties is studied in order to find a maximum value for the permittivity at the Curie-temperature.

7.2 Experimental

7.2.1 Powder preparation

- Mixed oxide powders are prepared by mixing the appropriate amounts of ZrO_2, TiO_2 and $BaCO_3$ followed by ball-milling in isopropanol, drying and calcination for 5 hours at 1200°C. Both heating and cooling rates are 5°C·min^{-1}. After calcination the powder is deagglomerated in cyclohexane, dried and finally ball-milled again in isopropanol.

- The so-called peroxo-oxalate method is based on the complexation of zirconium, titanium and barium with hydrogen peroxide and oxalic acid at pH 9 in an aqueous environment. The method is described in more detail elsewhere [8,9].

- A hydrothermally prepared powder is obtained from Sakai[*]. This powder was ball-milled for three hours in isopropanol to prevent irregular compaction.

All three powders contain a slight excess of titanium, which promotes grain growth by liquid phase formation.

7.2.2 Sintering experiments

Ceramic discs of 15 mm in diameter and 8 mm thickness are obtained by pre-pressing uniaxially at 80 MPa and subsequently isostatical pressing at 400 MPa. The compacts were sintered at temperatures of 1250-1450°C with different sintering times. Out off the ceramic body obtained, discs were sawn with a thickness of 0.5 mm and a diameter of 5 mm. The remainder was polished, thermally etched at 30°C below sintering temperature in a nitrogen atmosphere and used for SEM analysis.

7.2.3 Characterisation and dielectric measurements

The chemical composition of the calcined powders is measured by XRF using a Philips PW 1480/10 X-ray spectrometer. Density measurements are performed with the Archimedes technique using mercury. The microstructure of the ceramics was studied by SEM (Jeol JSM-5800). Chemical homogeneity of ceramics was measured with X-ray line broadening (Philips X'pert-1) on basis of the [2,2,0] peak.

---

[*] Sakai Chemical Industry Co., Ltd, Japan.

The sintered discs (5 mm ϕ by 0.5 mm thickness) were provided with a thin Cr/Ni-Au layer by means of evaporation. Dielectric measurements were performed at 1 kHz and 1 V using a Hewlett Packard 4274A multi-frequency LCR meter.

7.3 Results and Discussion

7.3.1 Annealing

As mentioned before, Hennings et al. [2] stated that internal stress is the major reason for normally observed diffuseness of the phase transition. To verify this, dielectric measurements of a number of samples were taken before and after an annealing step. The annealing step consist of the heating of a sample to 200°C, for 3 hours and then cooling the sample with 0.2°C·min^{-1}, which should reduces the amount of stress in this type of ceramics. Note that the cooling rate is twenty times slower than the cooling rate used by calcination and that during cooling the phase transition from cubic to rhombohedral occurs. This experiment was conducted with several samples that were sintered under various conditions. The effect of the annealing step is shown in *table 1*.
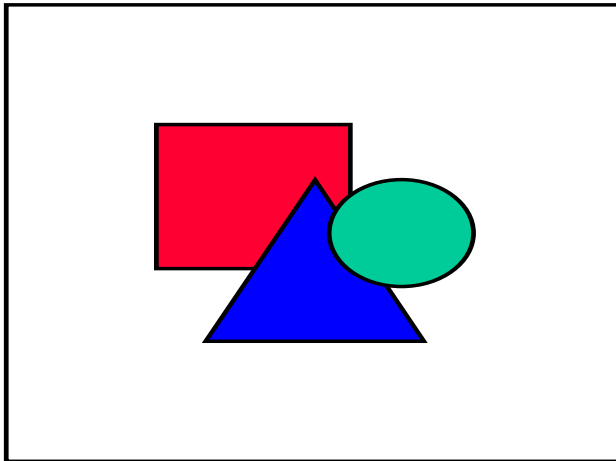

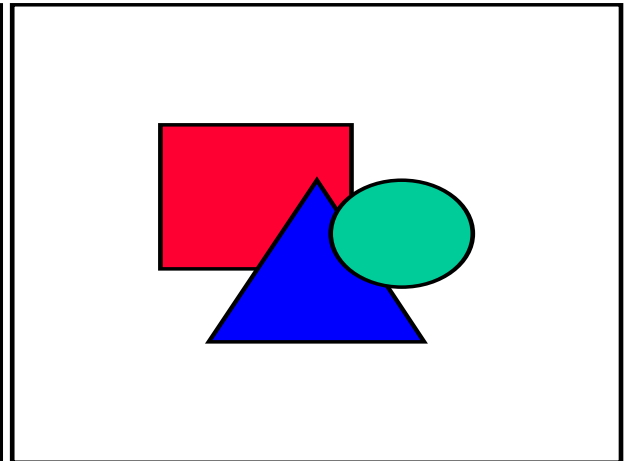*Figure 2: SEM micrograph, liquid phase sintering, step by step formation mechanism of grains.*

Figure 3: SEM micrograph, detail of anomalous grain growth.

Table 1: Effect of an annealing step on the dielectric properties, S = hydrothermal, M = mixed oxide A/B, A = sintering temperature (°C), B = sintering time (h), width is based on width permittivity versus temperature curve at ½ height.

Sintering Condition	Before			After			$\varepsilon_{r,max,before}/\varepsilon_{r,max,after}$
	$\varepsilon_{r,max}$	Curie-Temp.(°C)	Width (°C)	$\varepsilon_{r,max}$	Curie-Temp(°C)	Width (°C)	
S 1350/15	18415	89.7	40	20425	89.8	30	1.1
S 1500/15	40929	87.2	10	42371	87.3	10	1.03
M 1350/15	34282	88.7	20	36398	88.8	20	1.06
M1500/15	28876	86.1	20	30258	86.2	20	1.05

In this table it is visible that samples which are annealed have a maximum permittivity ($\varepsilon_{r,\ max}$) which is around 5% higher than the maximum permittivity of samples which have not been annealed. This emphasises the effect of the mechanical stress on the maximum permittivity. No relation could be established between the width of the permittity versus temperature peak and the presence of the annealing step.

7.3.2 Grain size

When the relation between the grain size and the maximum permittivity at the Curie-temperature is considered, a number of aspects is important. First of all the titanium ions in the ceramic must be polarised instantaneously. Second, the grains must be as large as possible to stimulate domain formation. Since more domains can be formed in large grains it is expected that a relation exist between the grain size and the permittivity.

Table 2: Dielectric properties of ceramics with incomplete anomalous grain growth, S = hydrothermal powder (not premilled), M = Mixed Oxide, Samples were sintered for 15h. 2°C·min $\uparrow$, 2°C·min$\downarrow$.

Sintering temp.	$(\varepsilon_{r,max})$	Tanδ
S 1350	31037	0.0082
S 1400	34668	0.0087
M 1350	15974	0.0067

7.3.2.1 Microstructural homogeneity

Large grains can be obtained with li-quid phase sintering. In case of barium titanate liquid phase sintering is cha-racterised by rapid grain growth of only a small number of grains. Liquid phase sintering is possible when a small excess of titanium is present in the compact. The excess titanium reacts with barium titanate to form $Ba_6Ti_{17}O_{40}$,

which forms a eutectic melt at 1317°C [11]. In *figure 2* it is visible that grains formed after liquid phase sintering are build step-wise out of thin layers, what is believed to be crystalline barium titanate. In *figure 3 and 4* it is visible that out of a matrix with rela-tive small grains larger grains are formed by consuming the smaller grains. In the final stage of sintering, when no more small grains are present, a homogeneous microstruc-ture is obtained. The extent of conversion to large grains depends primary on the tita-nium content and the sintering temperature [12].

Because of the assumed relation between grain size and the maximum permittivity, it is expected that ceramics that consist partially out of small grains contain a considerable amount of stress. In *table 2* the permittivity and dielectric loss of three samples, which have an irregular microstructure are given. The values obtained for the hydrothermal prepared powder are typical for ceramics with a homogeneous microstructure. The value for the mixed oxide ceramics is considerably smaller than that of ceramics with a homogeneous microstructure. The reason for the high value of the maximum permit-tivity in case of the hydrothermal ceramics is not clear.
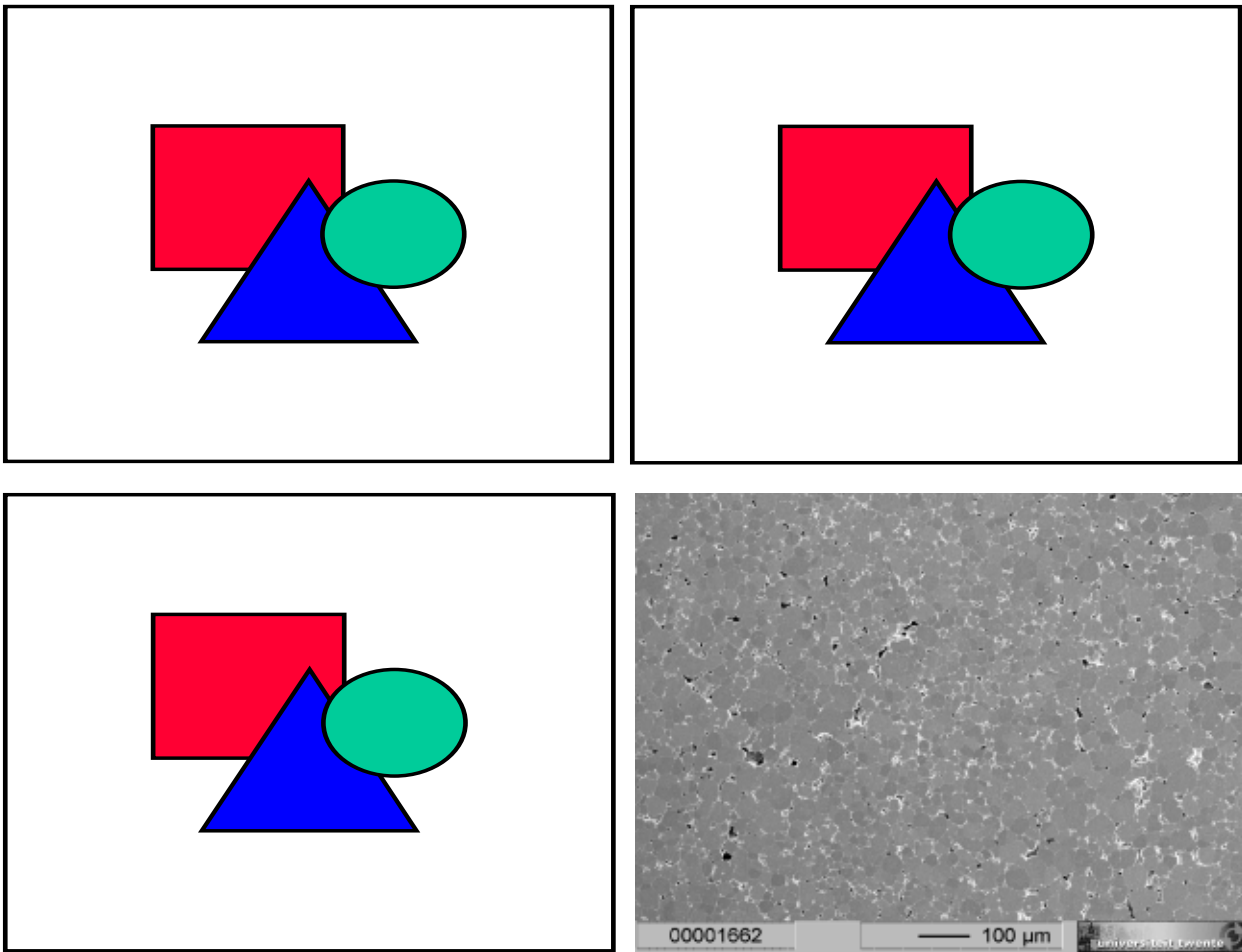
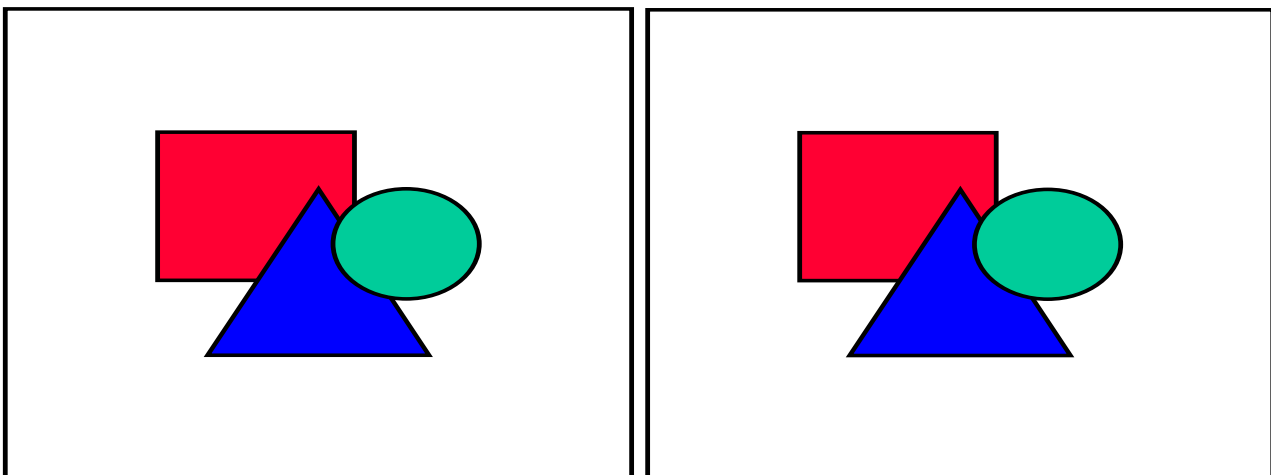*Figure 4:   Increase of the volume fraction of large grains with increasing sintering temperature.*

Figure 5:   SEM micrograph, pores as a result of fast grain growth.

Figure 6:   SEM   micrograph,   microstructure obtained with slow growing rate.

Table 3: Composition of the calcined powders as meas-
ured with XRF, measurement error around 1%.

Powder	Ba	Ti	Zr	(Ti+Zr)/Ba
Hydrothermal	1.000	0.913	0.100	1.012
Peroxo-oxalate	1.000	0.914	0.092	1.004
Mixed oxide	1.000	0.914	0.103	1.017

7.3.2.2 Large grains

Since the average surface energy in large grains is small compared to that of small grains, grain growth is relatively slow after the conversion to larger grains. In order to have a homogeneous microstructure that consists of exceptionally large grains it is necessary to have a limited amount of grains or nuclei growing in the liquid phase step. However, Hennings et al. stated that the discontinuous grain growth can not be effectively controlled by simple variations in sintering temperature, sintering time or modification of the chemical composition [11].

The amount of titanium excess must be sufficient to create a liquid phase around the entire grain. Hennings et al. found that 1% titania excess is sufficient to ensure complete wetting [11]. On the other hand the B-site excess[*] may also not be too large, because the titanium oxide rich phase reduces the maximum permittivity of the ceramic. In *table 3* it can be seen that the amount of titanium present in the three different calcined powders is comparable. The zirconium concentration, however, is the lowest in the peroxo-oxalate powder. It was found with SEM that grain growth was insufficient for the peroxo-oxalate ceramics, probably due to insufficient wetting, therefore, a new batch of powder was prepared with a large B-site excess. This titanium and zirconium rich peroxo-oxalate powder resulted in a complete dense ceramic with large grains.
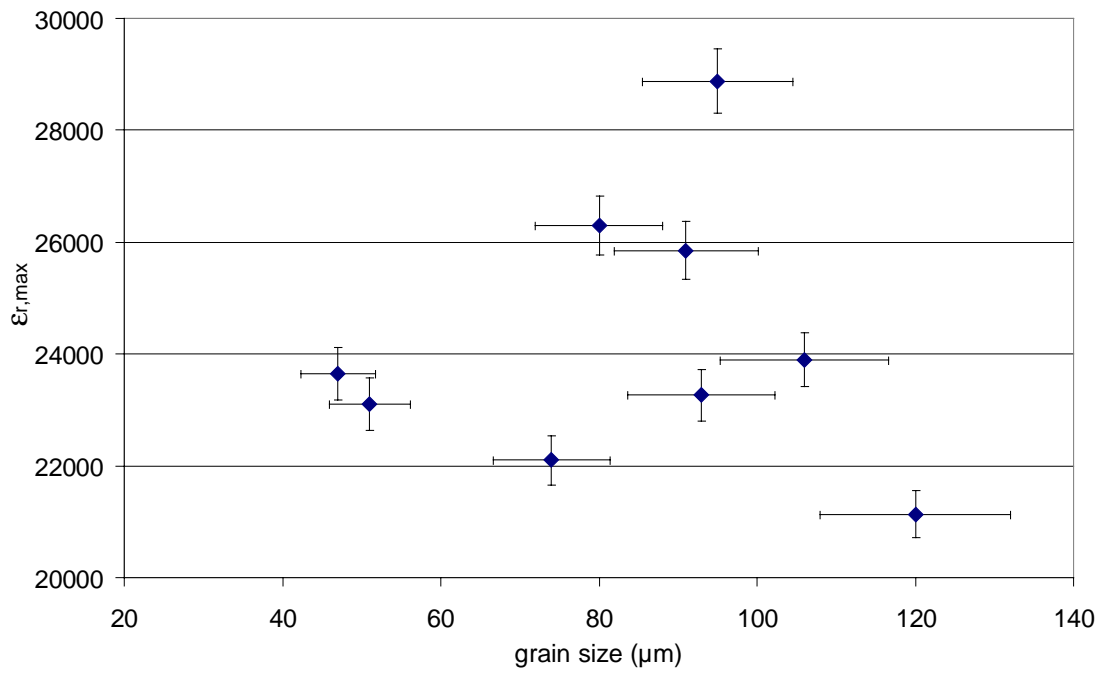
---

[*] B-site excess: ([Ti]+[Zr])/[Ba].

Figure 7: Mixed Oxide, grain size dependence of maximum permittivity, no relation could be observed between $\varepsilon_{r,max}$ and the grain size.
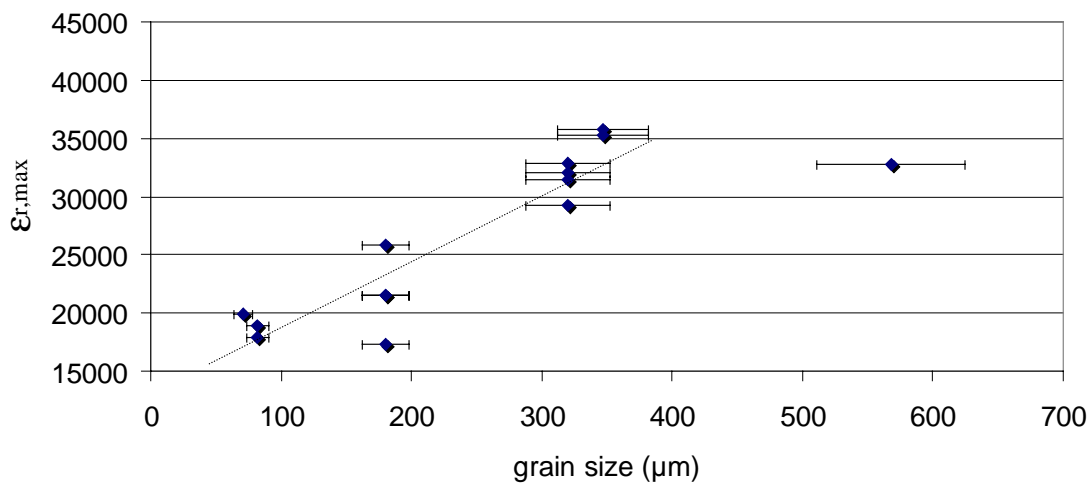

Figure 8: Hydrothermal, grain size dependence of maximum permittivity.

As can be seen in *table 3*, In case of the mixed oxide powder the B-site excess is somewhat larger than in the hydrothermal powder. This B-site excess, however, is mainly due to a change in the zirconium content. The effect of zirconium is not well known. Note that the amount of zirconia at the grain boundaries is limited and that the effect of zirconium, incorporated in $BaTiO_3$ on the material properties around the eutectic temperature is small.

The average grain size in mixed oxide ceramics is smaller than this average grain size in hydrothermal ceramics sintered under the same conditions. The small grain size can be explained by the fact that an increase in titania excess reduces the grain growth [11]. When an abnormal grain grows it consumes grain boundaries which contain an excess of titania. The amount of titania associated with these boundaries is redistributed along the newly formed grain boundaries and the bulk, which will, therefore, give rise to a increase in titania concentration along the grain boundaries [12]. Because a high concentration titania in the grain boundary reduces the grain growth, the grain growth rate is reduced or even stopped. Since the mixed oxide powders have a large B-site excess, the reduction in grain growth will take place more rapidly than in ceramics prepared with either the peroxo-oxalate or the hydrothermal powder.
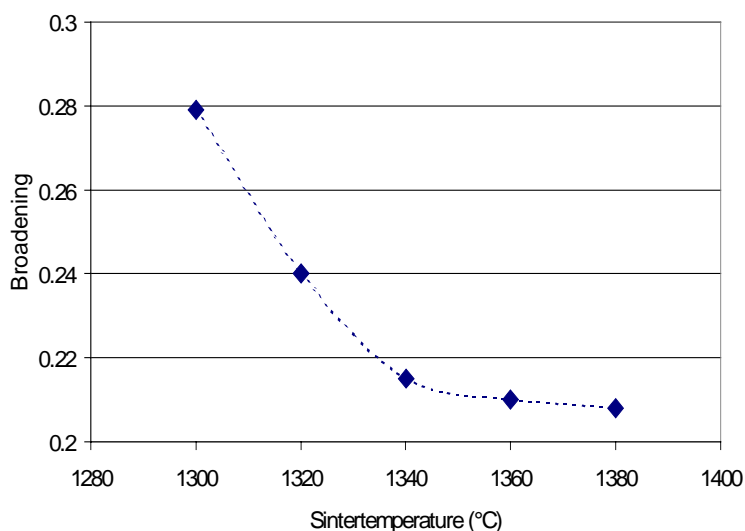

Figure 9: XRD broadening as function of sintering temperature, mixed oxide ceramics.

Liquid phase sintering has the disadvantage that pores are introduced in the grain bulk due to high grain growth rates, as is shown in *figure 5*. These so called interstitial pores are difficult to remove. In order to prevent these pores a slower growing rate is used, which is accomplished by a high heating rate during sintering in the region 1300 to 1400°C. To obtain large grains with these fast heating rates, a long sintering time (360 h.) must be used. The fast heating rate, however, results in a lower density and a smaller average grain size, compared to the average density of the samples sintered with fast growing rates. With the fast heating rate the pores are not positioned interstitially in the ceramic, but as is visible in *figure 6* are now located at the grain boundaries. The average grain size in ceramics prepared with the hydrothermal powder is 31 µm, which is very small in comparison with the slow heating rate samples. The maximum permittivity of the ceramic sintered at fast heating rate is lower in comparison to the maximum epsilon of samples sintered with slow heating growing rates, whereas the values of the dielectric loss are comparable. Sintering with a fast heating rate is not successful, because no increase in density is achieved. Still, this way of sintering might be interesting when the sinter forging is used, because then pores located at grain boundaries are more likely to densify than interstitial pores.

Since the growing rate by solid state diffusion is very slow in barium titanate ceramics it is not expected that with the slow growing rate grains can be obtained with a size larger than 100 µm. Note that the diameter of the grains is proportional with sintering time [11]. This relation is only valid when the growing of the large grains occurs by
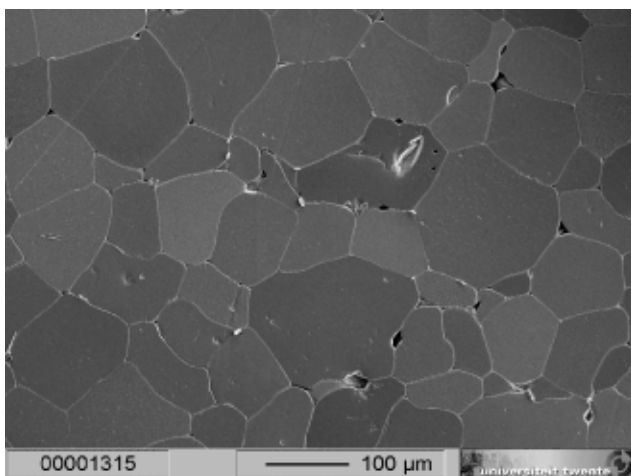

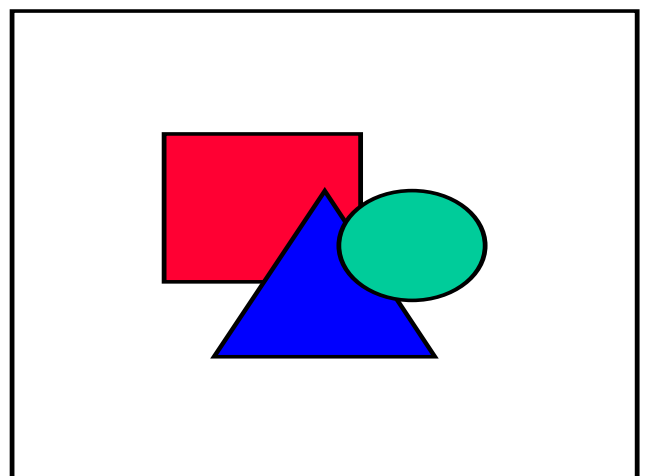Figure 10: SEM Micrograph, hydrothermal, sintered at 1400°C.

Figure 11: SEM micrograph, hydrothermal, sintered at 1500°C.

consuming small grains from the matrix. However, when interaction is present with other growing large grains, the growing rate is reduced [12].

7.3.2.3 Effect of grain size

Figure 7 shows the relation between the grain size and the maximum permittivity for the mixed oxide samples. The average values for maximum permittivity in case of mixed oxide prepared ceramics is higher than values obtained for hydrothermal prepared ceramics. As is visible in *figure 7* no clear relation could be established between the grain size and the maximum permittivity.

In *figure 8* it is visible that for the hydrothermal prepared ceramics up to 400 µm a slight increase in dielectric constant with grain size is present. The maximum permittivity of a sample with an average grain size around 580 µm is, however, approximately the same as the maximum permittivity found for the ceramics with grain sizes near 400 µm. This can be explained by the fact that at these large values for the grain sizes, the grain size is probably no longer the limiting factor for domain formation. After all, the ratio between the bulk and the surface of the grains hardly changes for these large grain sizes.
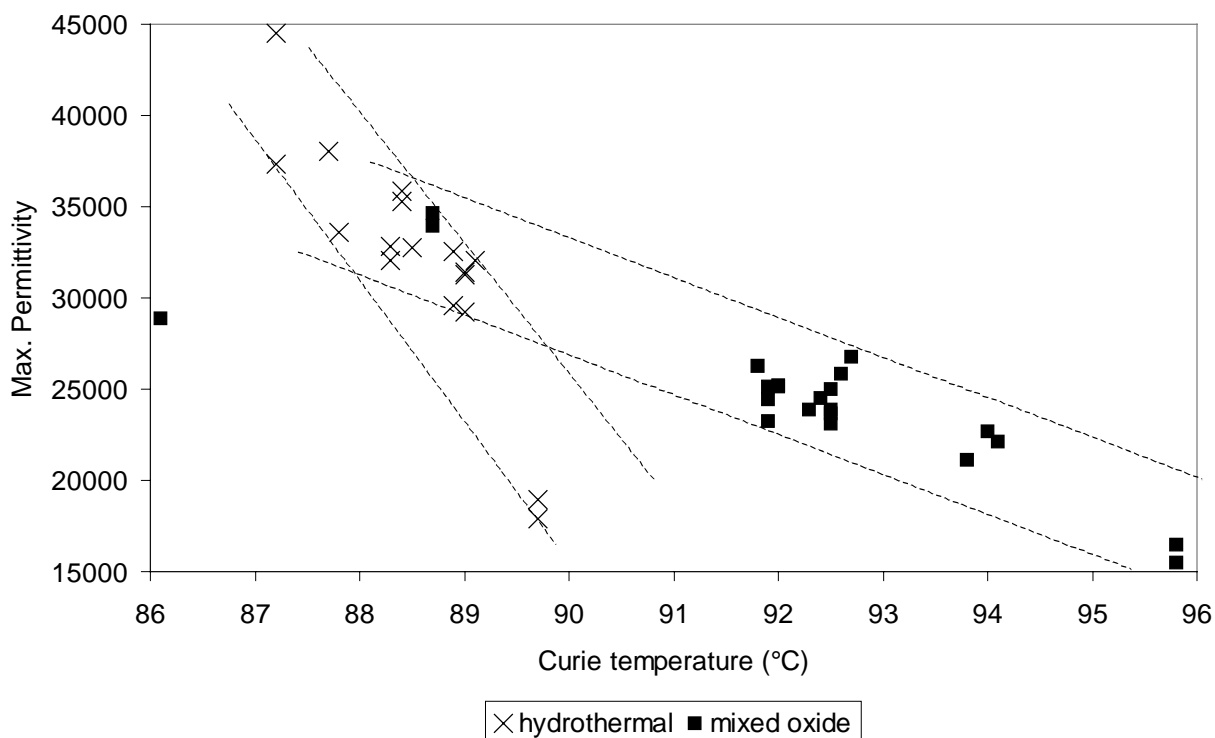

Figure 12:   Curie-temperature versus maximum permittivity for samples sintered under various conditions.

7.3.3   Chemical homogeneity

For the lamp starter application high sintering temperatures are required. This high temperature will induce diffusion, which rules out much of the differences in chemical homogeneity of the green compacts. The relation, for this type of application, between the chemical homogeneity and the maximum permittivity is therefore doubtful [2,3]. This hypotheses is supported by XRD measurements of ceramics sintered in the range of 1300 to 1380°C. As depicted in *figure 9*, the broadening as measured for the [2,2,0] peak first decreases with sintering temperature after which it levels off. Broadening is, amongst others, the result of stress, crystallite size and chemical homogeneity. It is further assumed that the crystallite size has no influence on ceramics consisting of large grains, while the amount of mechanical stress remains constant or decreases. One has to bear in mind that the average grain size changes as can be seen in *figure 4*. It is not known to what extent this change in grain size influences the amount of broadening of the XRD signal. However, the decrease in broadening as measured with XRD is likely to originate at least partially from the increased chemical homogeneity at higher sintering temperatures.

In *table 4* it can be seen that mixed oxide samples sintered at 1500°C have a higher value for the dielectric constant than samples sintered at lower temperatures and approximately the same grain size, see *figure 10 and 11*. This increase is observed for both the mixed oxide ceramics as well as for the hydrothermal ceramics and might be due to small differences in the chemical homogeneity. However, no suitable determination techniques are available to determine differences (if any) in chemical homogeneity in barium titanate ceramics sintered at high temperatures (see also chapter 6). No solid conclusions, therefore, can be drawn about the reason for the increase in dielectric maximum for ceramics prepared at a sintering temperature of 1500°C.

Another indication concerning the role of the chemical homogeneity is the Curie temperature. Neirman stated that when a deviation of the averaged concentration occurs, there is no averaging of symmetric volume element permittivity [5]. Because below and above the Curie-temperature different relations exist for the temperature dependence of the permittivity this change in concentration will lead to a shift in the Curie-

temperature. In this case a more homogenous composition will lead to a lower Curie temperature.

- $\varepsilon = k$ for $T < T_c$
- $\varepsilon = C/(T-T_0)$ for $T \geq T_c$

In these equations, k and C are constants and T_0 is the Curie-Weiss temperature.

Neirman stated that the broadening was due to differences in chemical composition. One has to bear in mind, however, that not only chemical inhomogeneity creates broadening of the $\varepsilon_r(T)$ signal, mechanical stress does also. Since the relation described above accounts for broadening in general, a reduction in the amount of stress should also result in a decrease of the Curie-temperature. Because a relation exists between broadening and the maximum permittivity, a relation between the height of the maximum permittivity and the Curie-temperature must exist. It is visible in *figure 12* that higher values for the maximum permittivity were obtained with ceramics with low Curie-temperatures. From *table 1*, however, it can be derived that the annealing step has no influence of the Curie-temperature of the ceramic. After all, the annealing step reduces the amount of mechanical stress and therefore reduces broadening. Therefore, the relation between stress and Curie-temperature remains unproven.

Table 4: Results of dielectric measurements on mixed oxide ceramics. Samples were sintered with various temperature profiles. Grain size is averaged and obtained by SEM and corrected according to Mendelson [13]. Temperature profile, 2/1400/15h = heating rate (°C·min⁻¹)/ sinter. temp.(°C)/ sinter. time.

Sinter profile	$\varepsilon_{r,max}$	Grain size (µm)	Curie-temp (°C).	tanδ
2/1300/0.5/1400/15h	24207	106	92.4	0.0061
2/1350/0.2/1400/15h	21134	120	93.8	0.0082
1/1400/30h	26292	98	92.6	0.0085
2/1400/15h	25729	80	91.8	0.0080
2/1450/15h	23835	93	91.9	0.0090
2/1500/15h	28876	95	86.1	0.0116

7.3.4 Maximum Permittivity

Because the application of lamp starters requires an extreme high value for the maximum permittivity at the Curie-temperature it is interesting which ceramic under which conditions results in the highest permittivity, see *table 5*. It is remarkable that sintering at 1500°C results in the highest value for both mixed oxide and hydrothermal ceramic. The peroxo-oxalate was not yet tested with this high sintering temperature. No difference in density or microstructure can, however, be observed between the ceramics sintered at 1500°C and ceramics sintered at lower temperatures. It is interesting that much larger grain sizes obtained by slow heating rates do not result in higher values for the dielectric constant. Apparently grain size is only important to a certain extent. When the grain size exceeds a certain critical value other factors play a larger role in determining the maximum permittivity at the Curie-temperature. The lower value for the maximum permittivity in case of the mixed oxide prepared ceramic might be the result of a higher content of titania and zirconia in the ceramic.

The maximum value obtained for the peroxo-oxalate prepared ceramic is somewhat lower than the value found for the hydrothermal ceramic. Since in this case again a comparable microstructure is observed, but it is not clear what causes the difference in permittivity. Note that it might be interesting to see what the effect is of sintering the peroxo-oxalate sample at 1500°C, but with a slow heating rate.

7.4 Conclusions

The grain size of ceramics with a titania excess of about 1.5% is the largest when the heating rate is minimal e.g. 0.2°C·min^{-1}. A high sintering temperature is more important to a certain level for obtaining an extreme high value for the maximum permittivity than for obtaining a large grain size. This is caused by the fact that sintering at 1500°C with a heating rate of 2°C·min^{-1} results in the highest value for the permittivity whereas only a grain size of 160 µm is obtained. A grain size up to 300 µm can be obtained, but this results in a lower maximum permittivity. From this observation, it can be concluded that in that case chemical homogeneity or possibly another aspect plays a role in determining the maximum permittivity while the role of mechanical stress is less pronounced.

Table 5: Maximum values for the permittivity obtained for ceramics prepared from three different powders.

Preparation method	Sintering profile	Grain size (µm)	$\varepsilon_{r,max}$
Peroxo-oxalate	1200/0.5/1400/5h	150	40410
Mixed oxide	1500/15h	958	34631
Hydrothermal	1500/15h	162	44526

The effect of the stress on the Curie-temperature is not clear. A higher value of the maximum permittivity is related to a lower value of the Curie-temperature. An annealing step, however, has an effect on the height of the maximum permittivity, but it has no influence on the Curie-temperature as observed.

Another indication that stress sometimes plays a minor role is obtained from the permittivity values of ceramics with an irregular microstructure, i.e. with small grains still present after sintering. For hydrothermal prepared ceramics in which no complete conversion to large grains is present, values for the maximum permittivity are obtained which are comparable to those of ceramics with homogeneous microstructure. Contrary, a relation is found between the maximum permittivity and the grain size in case of the hydrothermal prepared ceramic, which is in accordance with the stress theory according to Hennings [2,3].

An important factor for determining the maximum permittivity, next to the chemical homogeneity and the mechanical stress, is the composition of the powder. It is expected that by optimisation of the titanium content in the mixed oxide powder, the maximum permittivity of the ceramic can be increased to values comparable to those in hydrothermal and mixed oxide ceramics. The statement that in mixed oxide ceramics in comparison with wet-chemical prepared ceramics a lower chemical homogeneity is present, is not valid for ceramics where the material is homogenised by diffusion, which takes place as a result of high sintering temperatures.

7.5 References

1. S. Iwaya, H. Masumura, Y. Midori, Y. Oikawa and H. Abe, United States Patent, 4,404,029, "Non-linear polycrystalline barium titanate dielectric element".
2. D. Hennings and A. Schnell, "Diffuse ferroelectric phase transitions in $Ba(Ti_{1-y}Zr_y)O_3$ ceramics," *J. Am. Ceram. Soc.*, **65** [11] (1982) 539-544.

3. D. Hennings, "Barium titanate based ceramic materials for dielectric use," *Int. J. High. Tech. Ceram.*, **3** (1987) 91-111.

4. R. McSweeney, K. Zuk and D. Williamson, "Square loop Ba(Ti,Zr)O$_3$ capacitors on alkoxide derived (Ti,Zr)O$_2$ powders," in Proceedings of the first international conference on ceramic powder processing science, Orlando, Florida (1987).

5. S.M. Neirman, "The Curie point temperature of Ba(Ti$_{1-x}$Zr$_x$)O$_3$ solid solutions," *J. Mater. Sci.*, **23** 3973-80 (1988).

6. S. Kazaoui and J. Ravez, "Dielectric relaxation in Ba(Ti$_{0.8}$Zr$_{0.2}$)O$_3$ ceramics," *J. Mater. Sci*, **28** 1211-19 (1993).

7. T.N. Verbitskaja, G.S. Zhdanow, Y.N. Venevtsev and S.P. Soloviev, "Electrical and X-ray diffraction studies of the BaTiO$_3$-BaZrO$_3$ system," *Sov. Phys.-Cryst.*, **3** [2] 182-92 (1958).

8. S. van der Gijp, A.J.A. Winnubst and H. Verweij, "An oxalate-peroxide complex used for the preparation of doped-barium titanate," *J. Chem. Mater.*, **8** [5] 1251-54 (1998).

9. S. van der Gijp, A.J.A. Winnubst and H. Verweij, "Peroxo-oxalate preparation of doped-barium titanate," Accepted for publication in *J. Am. Ceram. Soc.*.

10. P. Phule and S.H. Risbud, "Low-temperature synthesis and processing of electronic materials in the BaO-TiO$_2$ system," *J. Mater. Sci.*, **25** 1169-83 (1990).

11. D.F.K. Hennings, "Control of liquid-phase-enhanced discontinuous grain growth in barium titanate," *J. Am. Ceram. Soc.*, **70** [1] (1987) 23-27.

12. P.R. Rios, T. Yamamoto, T. Kondo and T. Sakuma, "Abnormal grain growth kinetics of BaTiO$_3$ with an excess TiO$_2$," *Acta Mater.*, **46** [5] (1998) 1617-23.

13. M.I. Mendelson, "Average grain size in polycrystalline ceramics," *J. Am. Ceram. Soc.*, **52** [8] 443-46 (1969).

8 Perspectives

In this final chapter of this thesis the perspectives are described for barium titanate related systems. Recommendations will be given concerning the further research for MLCC's and lamp starter materials.

8.1 Synthesis

There are numerous methods for the preparation of undoped barium titanate. The choice of preparation route is closely related to the type of application. High technology products contain few impurities or defects and are consequently expensive. Due to the high price the production cost of high technology ceramics may be considerable. For bulk ceramics, however, lower production costs are required since the price of the ceramic should be lower as well. Hence, it is necessary to develop more wet-chemical preparation methods suitable for the production of cheap inexpensive ceramics, but which still result in an improvement in the desired material properties.

Most methods described the synthesis of pure undoped barium titanate only. To obtain a ceramic with all dopants distributed homogeneously throughout the ceramic body, the introduction of zirconium before calcination is a requirement. The peroxo-oxalate synthesis as described in this thesis is suitable for the simultaneous precipitation of zirconium, barium and titanium by means of a peroxo-oxalate complex.

- It is expected that due to the high pH and the presence of the oxalate other elements, like for example calcium, can also be precipitated simultaneously and be incorperated homogeneously in a barium titanate powder. This makes the peroxo-oxalate method suitable for the production of powder for MLCC applications.

- An other advantage of the peroxo-oxalate method is that the process is conducted in air, hence no carbondioxide free atmosphere is required.

- The peroxo-oxalate method enables the production of large quantity. It is closely related with the oxalate process which is, amongst others, used by Philips (Uden, the Netherlands). Only small modifications to the oxalate process are necessary to perform the peroxo-oxalate process on industrial scale. The weight losses with this

process are only slightly higher, but on the other hand, precipitation can be performed at lower temperatures.

It is also possible to combine the peroxo-oxalate method with homogeneous precipitation or with emulsion technology. In the homogeneous precipitation case it is necessary to control the stochiometry of the powder to obtain an A over B ratio of 1. When this problem is solved, the improved morphology can result in a significant reduction in sintering temperature, which is of interest for MLCC application (see later).

The use of the peroxo-oxalate preparation or other wet-chemical preparation methods with emulsion technology is very promising. The emulsion technology is based on a preparation process in emulsion droplets. Due to the small dimensions of the reactor vessel the size of the particles in solution is very small. The water which is most of the times the reaction medium can be removed by azeotropic destillation, the result is a microelemulsion with very small particles. This microemulsion can be dropped on a surface by e.g. spin coating, due to the small particle size it is possible to sinter these materials even at room temperature. It is therefore very interesting to study the emulsion technology for the production of barium titanate. For the preparation of bulk ceramics this technique might be less useful because it is expected that the resulting powder will be expensive and highly agglomerated.

On of the demerits of the wet-chemical preparation method is the low yield. It is useful even for lab-scale experiments to develop continuous preparation methods.

8.2 Multilayer ceramic capacitor

The MLCC will probably remain the largest application for doped barium titanate. In order to obtain a reduction in ceramic layer thickness in the MLCC and consequently to obtain an increase of the capacity, wet-chemical powders have to be used instead of the used mixed oxide powders. As mentioned before, the peroxo-oxalate method is a good option for the preparation of such a wet-chemical prepared power. Still the degree of aggregation of powders prepared with the classical wet-chemical preparation methods and therefore also the peroxo-oxalate method need to be reduced.

When wet-chemical preparation methods are used, fine particles can be produced which can be used in combination with Solufill[tm] technology [*] to manufacture MLCC's with a

---

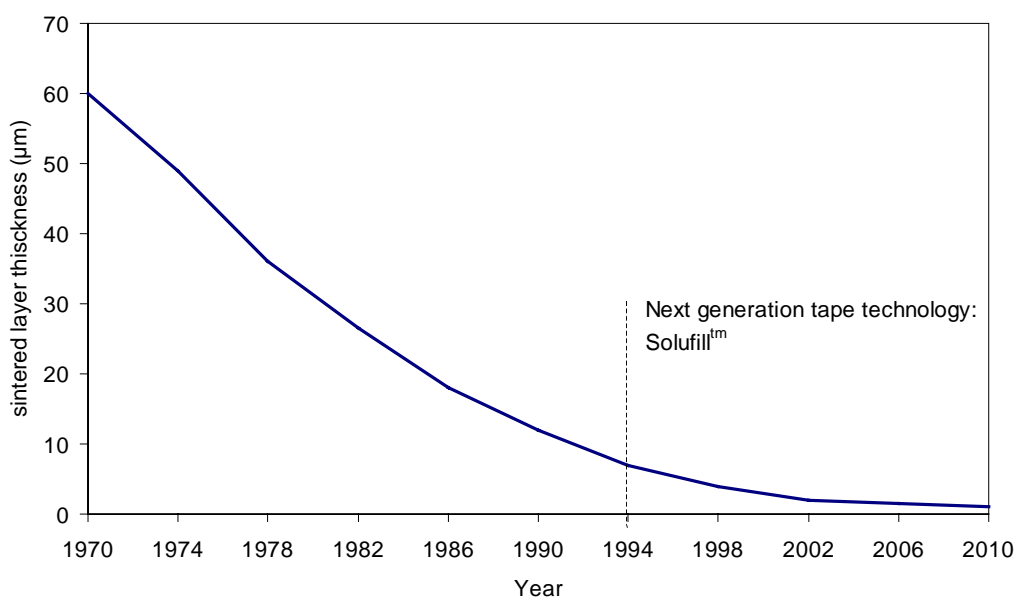[*] Solufill[tm] is a registered trademark of DSM Solutech.

Figure 1:   Trends and forecast of dielectric layer thickness reduction in MLCC market, copied from Höppener [1].

sintered dielectric layer thickness down to 1 µm, see also *figure 1* [1]. The question, however, arises, whether this layer thickness results in an improvement of the capacity. As mentioned in chapter 1, in case of barium titanate a relation exist between the height of the dielectric constant and the grain size. An optimum is found around a grain size of 0.8 µm. It seems, therefore, very difficult to prepare these thin layers with sufficient large grains. Note that no data concerning the permittivity of barium titanate with a grain size below 0.25 µm [3] is present. It is, therefore, interesting for MLCC applications to study the behaviour of barium titanate with a grain size below 0.25 µm. It might also be worthwhile to find other materials with a relatively high permittivity and a high breakdown strength which can be applied in layers with a thickness below 0.8 µm.

When a wet-chemical preparation method is combined with emulsion technology besides a reduction in grain size a reduction in sintering temperature can be obtained also. *Figure 2* shows the cost price of a standard MLCC. It can be seen that the internal and termination electrodes represent 30 to 60% of the overall costs. By a decrease in sintering temperature, instead of the Ag-Pd alloy a less noble metal or less of the more expensive Pd can be used. Both options will reduce the cost price of a MLCC remarkably.
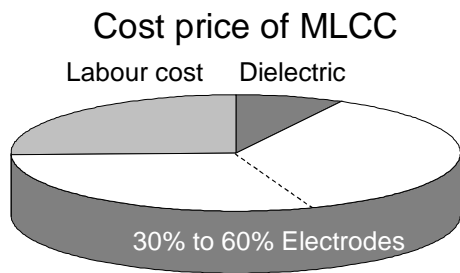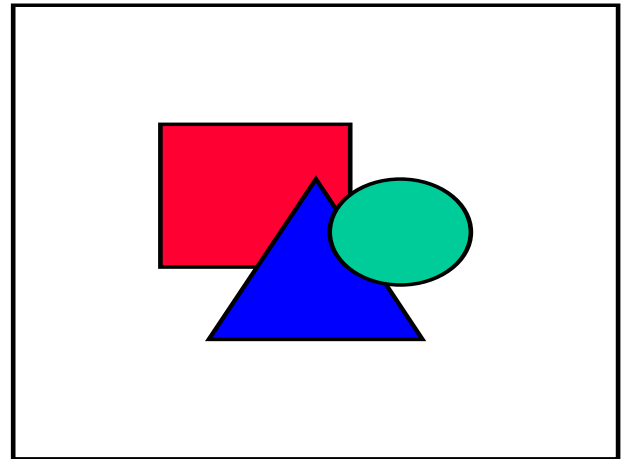
Figure 2: Overall costs of a MLCC [4].

Figure 3: *Near-percolative composite, which can be used as a highly effective capacitor.*

It can also be seen in *figure 2* that also labour costs are an important factor in the cost price of a MLCC. Again the cost price can be reduced remarkably when expensive and time consuming processing techniques like tape casting and stacking can be avoided. In order to do so a composite can be prepared which consist of an electrode material and a dielectric material. Such a composite is schematically drawn in *figure 3*. Investigations into those kinds of capacitors is still in an initial stage.

8.2 Application in lamp starters

The application of barium titanate in pulse-generating devices requires high sintering temperatures, which results in diffusion during sintering and consequently an increase in the chemical homogeneity of the ceramic.

As mentioned in chapter 6, it is difficult to determine differences between the level of chemical homogeneity in the various ceramics. The distribution of zirconium in a Sakai ceramic measured with SEM-EDX was not as good as compared to a peroxo-oxalate and a mixed oxide powder. It is doubtful whether, in case of the pulse-generating device, the chemical homogeneity of the ceramic has a large influence on the permittivity. Its is more likely that the chemical homogeneity in a preliminary stage of sintering influences the grain growth or densification, e.g. a local excess of titania inhibits grain growth. Therefore, a chemically homogeneous wet-chemical powder may still prove to be beneficial in comparison to a mixed oxide powder. To support this hypothesis and to

produce ceramics which consist of large grains with low internal porosity, it is necessary to study the influence of the chemical homogeneity on the grain growth and the densification behaviour.

With respect to the measurement of chemical homogeneity it can be stated that Auger spectroscopy is the most suitable technique because of its small spot size. Other techniques gave a more averaged picture of the concentration profiles in the ceramics. In future work it is a requirement to develop some sort of standard for analysing data on homogeneity. This standard must describe the relation between the position versus the intensity, which should also be applicable for other microstructural aspects, e.g. porosity distribution.

Stress was supposed to be the major reason for broadening of the permittivity versus temperature curve. In contradiction to a paper of Hennings [5], in two experiments no direct evidence for the effect of stress could be found.

1. Ceramics which consist out of small and large grains, the latter obtained by abnormal growth, have a maximum permittivity which is comparable to the permittivity of ceramics which consist completely out of large grains.

2. It was also difficult to establish a relation between grain size and maximum permittivity. Only in case of hydrothermally prepared powers for ceramic with a grain size up to 350 µm this relation was present. For mixed oxide powders no such relation was found.

To understand the role of mechanical stress it is necessary to measure the amount of mechanical stress in the ceramic samples in a more direct way. Bohanka et. al described a 3-point bending test which can be used to derive statements concerning the amount of internal stress in the material [6]. It might be interesting to correlate the results of such measurements with the maximum permittivity or grain size and to develop with this data a model to understand the behaviour of course-grained sized barium titanate.

8.4   References

1. R. Höppener, A. Daemen, "A New Tape Technology to Produce Multilayer Ceramic Capacitors," proceedings, in CARTS-Europe 1994
2. W. Sager, H.-F. Eicke and W. Sun, "Precipitation of nanometer-sized uniform ceramic particles in emulsions," *Coll. Surf.: Phys. Eng. A.* **79** (1993) 199-216.
3. J.C. Niepce, "Permittivity of fine grained $BaTiO_3$," pp 29-39 in *Electroceramics IV*, proceedings of the 4th international conference on electroceramics and applications. R. Waser, Aachen 5-7 September 1994.

4. A. Morell and J.-C. Niepce, "BaTiO$_3$ materials for M.L.C. capacitors applications," *J. Mater. Educ.*, **13** (1991) 173-232.

5. D. Hennings and A. Schnell, "Diffuse ferroelectric phase transitions in Ba(Ti$_{1-y}$Zr$_y$)O$_3$ Ceramics," *J. Am. Ceram. Soc.*, **65** [11] (1982) 539-44.

6. R.C. Pohanka, R.W. Rice and B.E. Walker Jr., "Effect of internal stress on the strength of BaTiO$_3$," *J. Am. Ceram. Soc.*,**59** [1-2] (1976) 71-74.