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An oxalate–peroxide complex used in the preparation of doped barium titanate

Sven van der Gijp,* Louis Winnubst and Henk Verweij

Laboratory for Inorganic Materials Science, Department of Chemical Technology, University of Twente, P.O.Box 217, 7500 AE Enschede, The Netherlands

A method is described for the preparation of homogeneously doped barium titanate, which can be applied in non-linear dielectric elements. Ba and Ti salts are dissolved, mixed with hydrogen peroxide and added to a solution of ammonium oxalate, resulting in the formation of an insoluble peroxo–oxalate complex. The presence of oxalate ions and a high pH are necessary for the formation after calcination of a stoichiometric and sinterable powder. To characterise the structure of the precipitating complex, the thermal decomposition of the complex is studied by means of XRD, d-TGA and FTIR. It is found that the precipitating complex is $BaTi_{0.91}Zr_{0.09}O_2(C_2O_4)\cdot 2H_2O$. The calcined powder prepared with the peroxo–oxalate method contains no second phase, in contrast to powders prepared with the oxalate method and the peroxide method.

Introduction

Doped barium titanate is used in a broad range of electroceramic devices. One example is a pulse-generating device, which can be applied in lamp starters in a fluorescent lamp.[1] For this type of application non-linear dielectric behaviour is needed. The required material properties for this type of application are: a high relative permittivity, a steep gradient of the polarisation *versus* electric field hysteresis curve and stable non-linear characteristics. These specifications can be met when the ceramic devices are made with a sinterable, 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 a bad chemical homogeneity. However, the mixed oxide process is easy to perform and when no evaporation occurs, stoichiometric powders can easily be obtained.

However, an improvement in homogeneity and morphology of the powder can be obtained when wet-chemical routes are utilised. This development will lead to better dielectric behaviour. Unfortunately, during wet-chemical 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.[4–6] In this process pure, undoped barium titanate is produced stoichiometrically by the formation and precipitation at low pH and 60 °C of a barium titanium oxalate complex. Another process for the preparation of barium titanate is the so-called peroxo process based on the formation and precipitation of titanium peroxide complexes at high pH and room temperature.[7] This process is described not only for $BaTiO_3$, but also for the production of titanium-rich materials ($BaTi_2O_5$) as well as barium zirconates and calcium and magnesium titanates.[7–11]

The peroxo–oxalate process described in this paper is a combination of the oxalate process and the peroxide process. This powder preparation method is suitable for the production of Zr-doped barium titanate ($BaTi_{0.91}Zr_{0.09}O_3$). Doping is possible due to the simultaneous presence of hydrogen peroxide and ammonium oxalate at high pH.

Note that the only difference between the peroxide process and the peroxo–oxalate process described here is the presence of oxalate, which changes the complexation properties of the titanium peroxo complex. The difference between the oxalate process and the peroxo process is that the oxalate process is conducted at high temperatures, low pH and in the absence of hydrogen peroxide. Hydrogen peroxide changes the solubility of titanium peroxo complex drastically.[7] However, neither the peroxide nor the oxalate method have been used up till now for Zr-doped $BaTiO_3$.

In order to obtain dielectric properties next to a single-phase polycrystalline material, a dense ceramic is required. Therefore, no aggregates in the powder may be present. The grain size of the final ceramic must be large, because large grains reduce internal stress and low values of internal stress result in a higher value for the dielectric maximum.[12]

In this paper the effect of oxalate on the powder properties is described. The precipitating complex in the peroxo–oxalate process and the thermal decomposition of the precipitating peroxo–oxalate complex are characterised by means of thermogravimetric analysis (d-TGA) and infrared spectroscopy (FTIR). The peroxo–oxalate method should result in a sinterable, homogenous and single-phase polycrystalline powder.

Experimental procedure

Powder and ceramic preparation

Peroxo–oxalate method. Titanium oxychloride (0.15 mol; 0.15 M) and zirconium chloride (0.015 mol; 0.015 M) were added to concentrated nitric acid (25 ml) and water. The total volume of the solution was 1 l. This solution was mixed with an aqueous solution of barium nitrate, prepared from barium carbonate (0.17 mol; 0.085 M) and nitric acid (50 ml; 0.25 M). The total volume of the mixed solution was 3 l. Finally, to this mixture hydrogen peroxide (30%, 100 ml) was added. This so-called ‘precursor’ solution was added dropwise to a solution of aqueous ammonia (0.5 mol) and different amounts of oxalic acid with a total volume of 5 l. During the addition of the precursor solution the pH was kept constant by the addition of small amounts of aqueous ammonia.

In this paper the ratio of oxalate ion concentration over the concentration of all the metal ions (Ba + Ti + Zr) present in solution is called x ($0 \leqslant x \leqslant 0.5$); note that when $x = 0$ this process is the peroxide process. All experiments were performed at room temperature.

After two hours stirring, the formed precipitate was filtered, washed with ethyl acetate, dried at 150 °C and calcined at

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†E-mail: s.vandergijp@ct.utwente.nl

900 °C. Powders were first pre-pressed uniaxially at 80 MPa and subsequently isostatically pressed at 400 MPa. All compacts were sintered at 1400 °C for 5 h; heating rate 2 °C min^{-1}, cooling rate 4 °C min^{-1}.

Oxalate method. Barium carbonate (0.1 mol) was carefully added to an aqueous solution of nitric acid (50 ml). To this solution titanium oxychloride (0.091 mol) and zirconium chloride (0.009 mol) were added. This solution had a volume of 2 l. This solution was added dropwise to a solution of oxalate (0.25 mol) in water (1 l) at a temperature of 60 °C.[4] After 2 h stirring the precipitated complex was separated by filtration and calcined at 900 °C.

Characterisation

The decomposition of the dried precipitate was studied by using TGA (Stanton Redcraft STA 625, heating rate 5 °C min^{-1} to 1000 °C), and Fourier-transform infrared spectroscopy (FTIR). FTIR measurements were performed *in situ* at temperatures from 200–800 °C at temperature intervals of 20 °C (with a holding [analysis] time at each temperature interval of a few minutes).

XRD measurements were performed using a Philips PW 1710 diffractometer with filtered Cu-Kα_1-radiation, $\lambda =$ 1.4508 Å. The chemical composition was measured with X-ray fluorescence spectroscopy (XRF, X-ray spectrometer, Philips PW 1480/10).

Particle size distributions were measured with a Microtrac X-500 (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 was revealed by etching at a temperature 30 °C below the sintering temperature in a nitrogen atmosphere. To study the influence of oxalate on the ligand structure of the complex, the difference in absorption maximum was measured for a solution at pH = 4, containing titanium and hydrogen peroxide, before and after the addition of oxalic acid. UV–VIS measurements were carried out with a Philips PU 8740 spectrophotometer.

Non-isothermal densification was studied on a Netzsch 410 dilatometer; heating rate 2 °C min^{-1}, cooling rate 4 °C min^{-1}, holding time 3 h. Density measurements were performed with the Archimedes technique using mercury.

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 some gas formation is observed, probably oxygen formed by the partial decomposition of hydrogen peroxide in the basic aqueous environment.

Influence of oxalate on powder properties

Fig. 1 shows XRD results of the calcined powders prepared with increasing oxalate content. It is clear that the amount of second phase in the calcined powder as determined by XRD depends on the oxalate concentration. The powder prepared according to the peroxide method ($x = 0$) contains secondary phases. The secondary phases present are mainly $BaTi_2O_5$ and $BaCO_3$. For increasing amounts of oxalate, the amount of these secondary phases decreases. At 0.50 molar equivalent oxalate no secondary phases are present and only the cubic perovskite phase is present.

In spite of the change in phase composition of the powders, XRF measurements indicate that there is no difference in composition between the powders prepared according to the peroxide method ($x = 0$) and the oxalate method ($x = 0.5$).

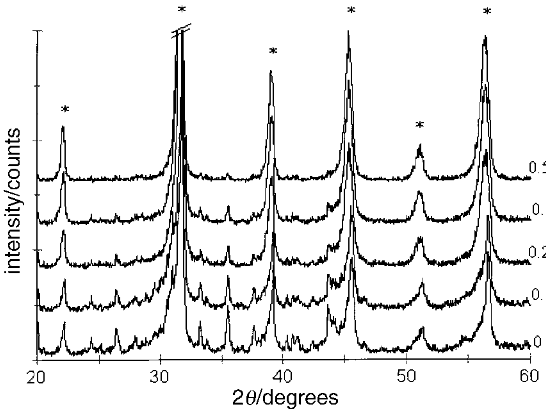

Fig. 1 XRD of calcined powder prepared with increasing amounts of oxalate, x, as indicated on the right; *denotes the (cubic) perovskite structure

Apparently, the presence of oxalate during complex formation results in a different structure of the final precipitated complex. Doping with Zr seems possible due to the simultaneous presence of oxalate and hydrogen peroxide.

When a Zr-doped $BaTiO_3$ calcined powder is prepared according to the oxalate method (in the absence of hydrogen peroxide and in acidic environment), secondary phases are detected too, mainly $BaZrO_3$, indicating that the oxalate method is not suitable for the preparation of $BaTi_{0.91}Zr_{0.09}O_3$.

Identification of the precipitating complex

The weight loss found from TGA, after calcination to a temperature of 1000 °C, for the dried precipitates prepared with the peroxide method ($x = 0$) is 20%. This corresponds to the theoretical weight loss found for the thermal decomposition of $BaTiO_2(O_2)\cdot 2H_2O$, the complex formed with the peroxide method,[7] to $BaTiO_3$. Note that both oxygen ligands in $BaTi(O_2)O_2\cdot 3H_2O$ are different.

When oxalate is introduced in the process, the weight loss increases to 31% for $x = 0.5$. Also the thermal decomposition behaviour changes when more oxalate is added in the process, as can be seen in Fig. 3 (later). In this figure the derivatives of the TGA (d-TGA) results are given for three precipitates prepared with $x = 0.125$, $x = 0.25$ and $x = 0.50$. It can be seen that with an increasing amount of oxalate in the reaction mixture the d-TGA signals change, especially at approximately 250 and 700 °C. Therefore, the addition of oxalate in the process results in the formation of a different precipitating complex as compared to the precipitating complex in the case of the peroxide method ($x = 0$).

Confirmation that such a change in ligand structure does occur in the presence of oxalate ions ($x > 0$), is provided by the shift of the absorption maximum of the complex. This shift takes place from 356 nm in the absence of oxalate to 392 nm in the presence of oxalate, as measured with UV–VIS spectroscopy in acidic aqueous environment.

To characterise the structure of the precipitating complex in the case of $x = 0.5$ FTIR measurements and TGA were performed *in situ* as a function of temperature in the range 1000–4000 cm^{-1}. The spectra for $x = 0.5$ are given in Fig. 2. IR signal 1 (at 3500 cm^{-1}) corresponds to water. It is clear that water is still present at temperatures up to 600 °C. Most of the water is removed at temperatures between 400 and 500 °C. Signal 2 (1700 cm^{-1}, a characteristic signal[13] at 1300 cm^{-1} is present but is however not visible in this plot) correspond to CO vibrations of an oxalate ligand.[14] These vibrations have disappeared at 500 °C. This means that this initial complex is no longer present above 500 °C. Peaks marked 3 (2500, 1750, 1500 and 1050 cm^{-1}) are attributed to

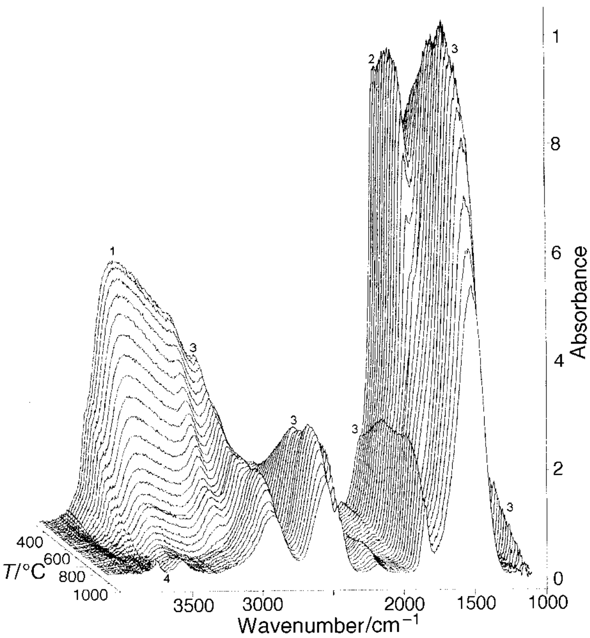

Fig. 2 Infrared spectra of the decomposition of the peroxo–oxalate complex (temperature intervals 20 °C), $x=0.5$. 1: water, 2: complex, 3: $BaCO_3$, 4: $Ti(OH)_x$

CO vibrations in (barium) carbonate.[13,14] The intensity of these signals first increases and reaches a maximum at 600 °C, after which the intensity decreases again. This indicates that the intermediate formed after decomposition of the initial complex consist at least partially of $BaCO_3$. The vibrations corresponding to $BaCO_3$ are still present at 800 °C. Finally, signal 4 ($3550\,cm^{-1}$) corresponds to OH vibrations of $Ti(OH)_x$.[15] This signal arises at temperatures above 700 °C. XRD analyses indicate the onset of crystalline perovskite formation at 800 °C, therefore the intermediate containing the $BaCO_3$ formed from the initial complex starts to decompose at this temperature.

FTIR analysis at 800 °C still shows the presence of $BaCO_3$. This was confirmed by room temperature XRD measurements, where perovskite as well as $BaCO_3$ signals were found after heating to 800 °C. XRD analysis of a powder calcined at 900 °C showed a 100% perovskite crystal structure. Note that the absence of barium carbonate at 900 °C could not be confirmed by FTIR measurements because the maximum temperature for the high-temperature FTIR equipment used is 800 °C.

Using the combined data of TGA, FTIR and XRD measurements the following structure is proposed for the precipitating complex ($x=0.5$): $BaTi_{0.91}Zr_{0.09}O_2(C_2O_4)\cdot 3H_2O$. The thermal decomposition mechanism of this complex is described below, a mechanism which is closely related to the decomposition mechanism for the complex formed with the oxalate method.[5]

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

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

$$[BaCO_3\cdot TiO_2] \xrightarrow{800\,^{\circ}C} BaTiO_3 + CO_2$$

In these reactions Zr is left out for reasons of simplicity, it is assumed that in this case Zr reacts in the same manner as Ti. It can be seen that the complex formed in the peroxo–oxalate complex ($x=0.5$) is very similar to the complex formed with the peroxide method ($x=0$), namely $BaTi_{0.91}Zr_{0.09}O_2(C_2O_4)\cdot 3H_2O$ instead of $BaTi_{0.91}Zr_{0.09}O_2(O_2)\cdot 3H_2O$. The theoretical weight loss for the proposed complex corresponds to the weight loss found with TGA.

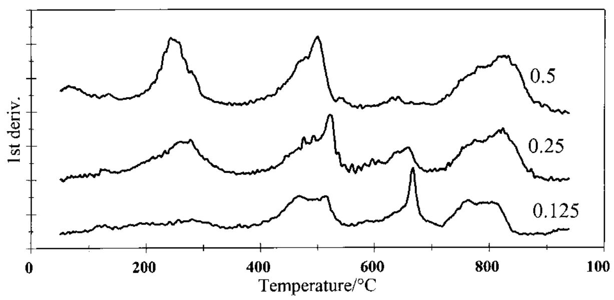

Fig. 3 d-TGA of dried precipitate prepared with increasing amounts of oxalate, x (0.25, 0.5 and 1)

The temperatures of the above reaction mechanism steps correspond to the three maxima in the d-TGA spectrum for $x=0.5$ in Fig. 3. Considering the FTIR and XRD data these temperatures can be regarded as onset temperatures for these reactions. The maxima in Fig. 3 found for lower concentrations of oxalate are a mixture of the maxima found for the decomposition of the peroxo–oxalate structure and those maxima found in the thermal decomposition of the peroxo complex as produced with the peroxide method ($x=0$) and described below.[7]

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

$$BaTiO_2(O_2)\cdot H_2O \xrightarrow{500\,^{\circ}C} BaTiO_2(O_2)\cdot H_2O$$

$$BaTiO_2(O_2) \xrightarrow{750\,^{\circ}C} BaO_2 + TiO_2\ (\text{rutile}) \rightarrow BaTiO_3 + 1/2O_2$$

Powder morphology and densification

The presence of ammonium oxalate also has an influence on the powder morphology. An increase in the oxalate concentration leds to a decrease in particle size (see Table 1). The smaller agglomerate size as determined from light scattering studies after ultrasonic treatment results in an increase of the green density as shown in Table 1.

In Fig. 4 a micrograph is given of a calcined powder prepared with the peroxo–oxalate method ($x=0.5$). It is clear that the powder consists of agglomerates, which in their turn consist of aggregates, with a size comparable to the size determined from light scattering measurements (1 µm). Within these aggregates smaller particles are visible. The average aggregate sizes of the various powders are given in Table 1.

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.

Dilatometer experiments on an isostatically pressed sample revealed a dense (95% rel. density) sample at a temperature of 1400 °C. The maximum densification rate was at approximately 1180 °C. A sample heated for 10 h sintered at 1400 °C had a grain size of 62 µm. High sintering temperatures are necessary

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

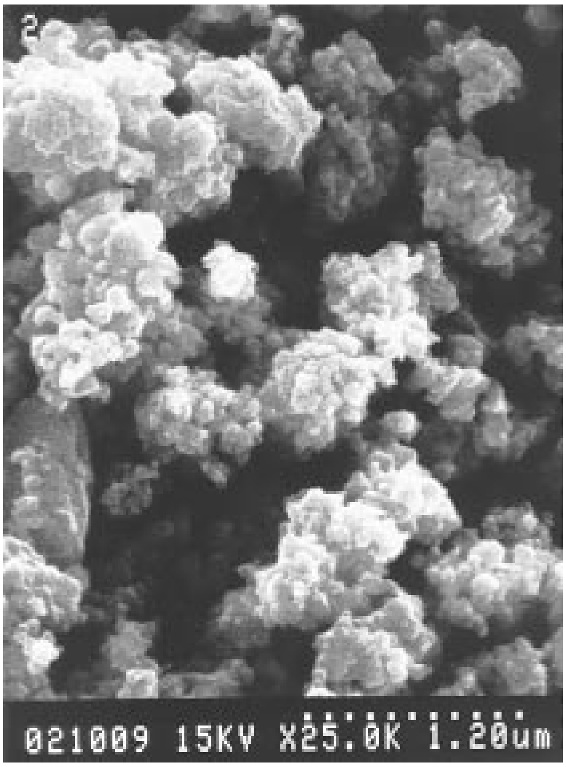

Fig. 4 SEM of calcined powder, magnification 25.000, $x=0.5$

to obtain the large grain sizes. Dielectric measurements show an ε_r value of 27000 at a temperature of 90 °C. At 70 and 110 °C the relative permittivity has 20% of its maximum value.

Conclusions

The peroxo–oxalate method with sufficient oxalate results in single-phase perovskite, $BaTi_{0.91}Zr_{0.09}O_3$, the optimum amount of oxalate in the process is $x=0.5$. The peroxide method ($x=0$) and the oxalate method result in the formation of a second phase. The presence of oxalate during the process ensures complete stoichiometric precipitation and an increasing amount of oxalate results in an increase of the green density. The precipitating complex in the peroxo–oxalate process is $BaTi_{0.91}Zr_{0.09}O_2(C_2O_4)\cdot 3H_2O$. The thermal decomposition of this complex is described. Finally, a calcined powder prepared using the peroxo–oxalate method ($x=0.5$) is homogenous and sinterable.

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