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Peroxide Route to Synthesize Calcium Titanate Powders of Different Composition

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Abstract

The calcium titanates $CaTiO_3$, $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$ can be synthesized by the wet chemical peroxide route. The first step of the preparation is the precipitation of peroxo-precursors of definite stoichiometry which are transformable into the corresponding titanates by thermal decomposition. The resulting ultra-fine, phase-pure calcium titanate powders have only a small impurity content. They are very sinter active above 1200°C. The rate of densification during sintering of compacts is improved in the sequence $Ca_3Ti_2O_7 < Ca_4Ti_3O_{10} < CaTiO_3$, considering the green densities, the densities at a given time and the theoretical densities of the titanates for the calculations. The phase $CaTi_4O_9$ can be obtained after thermal degradation of a corresponding peroxo-precursor at temperatures below 700°C. There are also indications of the formation of the phase $CaTi_2O_5$ below 700°C. A phase Ca_2TiO_4 can not be synthesized using the peroxide route.

Die Calciumtitanate $CaTiO_3$, $Ca_3Ti_2O_7$ und $Ca_4Ti_3O_{10}$ können mit der Peroxidmethode auf naßchemischem Weg synthetisiert werden. Der erste Präparationsschritt besteht in der Fällung von Peroxo-Precursors definierter Stöchiometrie, welche durch thermische Zersetzung in die entsprechenden Titanate überführbar sind. Die entstehenden ultrafeinen, phasenreinen Calciumtitanatpulver haben nur einen geringen Gehalt an Verunreinigungen. Oberhalb 1200°C sind sie sehr sinteraktiv. Berechnungen unter Einbeziehung der Ausgangsdichten, der Dichten nach bestimmten Sinterzeiten und der theoretischen Dichten der Titanate zeigen, daß Verdichtungsgeschwindigkeit beim Sintern von Preßlingen in der Reihenfolge $Ca_3Ti_2O_7 < Ca_4Ti_3O_{10} < CaTiO_3$ zunimmt. Die Phase $CaTi_4O_9$ ist durch thermischen Abbau des zugehörigen Peroxo-Precursors bei Temperaturen unterhalb 700°C zugänglich. Es gibt auch Indizien für die Bildung der Phase $CaTi_2O_5$ unterhalb 700°C. Eine Phase Ca_2TiO_4 ist mit der Peroxidmethode nicht darstellbar.

Les titanates de calcium $CaTiO_3$, $Ca_3Ti_2O_7$ et $Ca_4Ti_3O_{10}$ peuvent être synthétisés par chimie humide voie peroxyde. La première étape de la synthèse est la précipitation de précurseurs peroxydes de stoechiométrie définie, qui pourront ensuite donner les titanates correspondants par décomposition thermique. Les poudres de calcium de titanate résultantes, ultrafines et à haute pureté phasique, ont un faible taux d'impuretés. Elles sont très réactives au dessus de 1200°C. Le taux de densification pendant le frittage des compacts s'améliore suivant la séquence $Ca_3Ti_2O_7 < Ca_4Ti_3O_{10} < CaTiO_3$, en considérant pour les calculs les densités en crue, les densités à un moment donné et les densités théoriques des titanates. La phase $CaTi_4O_9$ peut être obtenue, après dégradation thermique d'un précurseur peroxyde correspondant, à des températures inférieures à 700°C. Nous avons également relevé des indications de formation de la phase $CaTi_2O_5$ en dessous de 700°C. La phase Ca_2TiO_4 ne peut être synthétisée par la voie peroxyde.

1 Introduction

Calcium titanates are interesting compounds especially because of their electrical properties. The phase equilibria in the CaO–TiO_2 system have been studied extensively and the existence of the compositions $CaTiO_3$, $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$ has

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been reported in the literature.[1-5] It has been found that the composition Ca_2TiO_4 is thermodynamically unstable towards decomposition to other phases.[6] There is also little information on the synthesis of $CaTi_2O_5$ and $CaTi_4O_9$ using a wet chemical route.[7,8] These compounds are said to be formed below 800°C by calcination of Ca and Ti containing precipitates.

$CaTiO_3$, with its perovskite structure, is a highly refractory compound which is resistant to corrosion by concentrated caustic soda solution. It is an n-type semiconductor on annealing at high temperatures under reducing atmospheres or by donor doping.[9-11] The structure of $Ca_3Ti_2O_7$ consists of double perovskite layers interleaved with CaO, whereas $Ca_4Ti_3O_{10}$ has triple perovskite layers interleaved with CaO.[3]

Although the physical properties of calcium titanates have been studied intensively, there is only a little information on the synthesis and on the sintering behaviour of phase-pure, high-purity $CaTiO_3$ or of the other titanate compositions. Calcium titanates are commonly prepared by the solid-state reaction of $CaCO_3$ and TiO_2 at temperatures above 1300°C. The effect of the reactivity of the starting materials on the sinterability of calcium titanate has been studied by Degtyareva and Verba.[12,13] They found that open porosity decreases with increasing sintering temperature, reaching 5·3% at 1600°C, when the most reactive starting compounds were used.

Wet chemical methods for the synthesis of $CaTiO_3$ are also known. It is formed by thermal degradation of precipitated calcium titanyl oxalate[14,15] or by heating of a catecholate complex at 600°C.[16] Fine $CaTiO_3$ powders consisting of 0·1–0·5 μm size crystallites can be prepared at 150–200°C by the hydrothermal method starting from hydrated titania gel and reactive calcium oxide suspended as an aqueous slurry in an autoclave.[17] These hydrothermally prepared $CaTiO_3$ powders are sinterable to high-density ceramics below 1400°C. On the other hand, homogeneous $CaTiO_3$ can also be synthesized by a modified Pechini method.[10,18]

Another synthesis to obtain high-purity $CaTiO_3$ is the peroxide route.[19,20] This synthesis occurs via the precursor $CaTiO_2(O_2).3H_2O$ using $CaCl_2$, $TiCl_4$, H_2O_2 and NH_3 as starting compounds.[21] The preparation is likewise possible by use of titanium tetraisopropoxide instead of $TiCl_4$.[22] Sintered densities as high as 98·3% of theoretical were obtained for the so-prepared $CaTiO_3$ powder treated in organic solvents and calcined at 800°C.

It is the aim of this paper to investigate the formation of further calcium titanate compositions like $Ca_3Ti_2O_7$ or $Ca_4Ti_3O_{10}$ using the peroxide method. Experiments for the synthesis of other compositions like $CaTi_2O_5$, $CaTi_4O_9$ or Ca_2TiO_4 are also described. In the case of the Ba–Ti–O system Ba_2TiO_4, $BaTiO_3$, $BaTi_2O_5$ and $BaTi_4O_9$, and in the case of the Sr–Ti–O system Sr_2TiO_4, $SrTiO_3$, $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ have been obtained by the peroxide route.[23-27] The precipitation of the calcium- and titanium-containing precursors, their thermal decomposition to the titanates and the characterization of both intermediate products and the final titanate powders as well as the results from sintering experiments are described in this communication.

2 Experimental Procedure

An aqueous solution of $CaCl_2 . 6H_2O$ and $TiCl_4$ (Ti concentration 0·8 mol/litre) was added rapidly at 10°C under argon into a larger volume (× 1·5) of a solution of H_2O_2 and ammonia in water. The molar ratios of $CaCl_2 . 6H_2O:TiCl_4:H_2O_2:NH_3$ used were 1:1:2·5:12 for $CaTiO_3$, 3:2:7:20 for $Ca_3Ti_2O_7$, and 4:3:10:30 for $Ca_4Ti_3O_{10}$. The conditions for the synthesis of $CaTiO_3$ have already been described in a former paper.[21] Experiments to synthesize the compositions $CaTi_2O_5$, $CaTi_4O_9$ and Ca_2TiO_4 were carried out in a similar manner using the molar ratios 1:2:2·5:24 for $CaTi_2O_5$, 1:4:2·5:50 for $CaTi_4O_9$, and 2:1:5:12 for Ca_2TiO_4. Light yellow amorphous precipitates were formed in all cases.

The precipitates were filtered, washed with water and then dried with H_2SO_4 in a desiccator. The resulting precursors were calcined at different temperatures up to 900°C.

The chemical analysis of the precursors and of the powders obtained after calcination for 1 h at 900°C was performed as follows. Titanium was determined gravimetrically, after precipitation with cupferron and annealing, as TiO_2,[28] and calcium was titrated complexometrically with thymolphthalexon as indicator.[29] The peroxide content was analysed iodometrically.

Thermal decomposition of the peroxo-precursors was investigated by thermogravimetry (TG) and differential thermal analysis (DTA). X-Ray diffraction measurements allowed the formation of the titanate phases to be located.

The calcium titanate powders calcined at 900°C for 1 h were mixed with a binder solution (65% H_2O, 25% glycerol, 10% PVA) in a mortar, disagglomerated for 20 min in a ball mill (Fritsch Pulverisette) and dried at 80°C before granulating through an 80 mesh sieve. The powders were pressed in the form of discs under a pressure of 125 MPa and sintered at 1200 and 1400°C under isothermal conditions. The densities of the disc-shaped specimens with an initial diameter of 10 mm and height of 5 mm were determined by measuring weights and dimensions at the beginning and after heating steps, utilizing an external micrometer.

3 Results

The results of the analysis of the dried precursors and of the powders obtained after calcination at 900°C are shown in Table 1. The peroxo-precursors for $CaTiO_3$, $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$ show a stoichiometric composition as well as the titanates. The reactions of the precursor formation can be described as follows:

$$CaCl_2 + TiCl_4 + H_2O_2 + 6NH_3 + 5H_2O \rightarrow CaTiO_2(O_2).3H_2O + 6NH_4Cl \quad (1)$$

$$3CaCl_2 + 2TiCl_4 + 2H_2O_2 + 14NH_3 + 9H_2O \rightarrow Ca_3Ti_2O_5(O_2)_2.4H_2O + 14NH_4Cl \quad (2)$$

$$4CaCl_2 + 3TiCl_4 + 4H_2O_2 + 20NH_3 + 12H_2O \rightarrow Ca_4Ti_3O_8(O_2)_2.6H_2O + 20NH_4Cl \quad (3)$$

The experiments for the formation of suitable peroxo-precursors for the preparation of $CaTi_2O_5$, $CaTi_4O_9$ and Ca_2TiO_4 can be summarized by the following equations:

$$CaCl_2 + 2TiCl_4 + H_2O_2 + 10NH_3 + 8H_2O \rightarrow CaTi_2O_4(O_2).4H_2O + 10NH_4Cl \quad (4)$$

$$CaCl_2 + 4TiCl_4 + 2H_2O_2 + 18NH_3 + 13H_2O \rightarrow CaTi_4O_7(O_2)_2.6H_2O + 18NH_4Cl \quad (5)$$

$$2CaCl_2 + TiCl_4 + H_2O_2 + 8NH_3 + 5H_2O \rightarrow Ca_2TiO_3(O_2).2H_2O + 8NH_4Cl \quad (6)$$

The TG, DTG and DTA curves of the thermal decomposition of the three precursors of reactions (1), (2) and (3) are shown in Fig. 1. $Ca_3Ti_2O_5(O_2)_2.4H_2O$ and $Ca_4Ti_3O_8(O_2)_2.6H_2O$ show a similar behaviour during heating. In a first step up to 300°C the water is evaporated (endothermic effect). The decomposition of the peroxide

Table 1. Analytical data for the peroxo-precursors and for the products obtained after thermal decomposition at 900°C (weight loss for 1 h at 900°C)

Component	(% *exp.*)	(% *calc.*)	(% exp.)	(% *calc.*)
	$CaTiO_2(O_2).3H_2O$		$CaTiO_3$	
Calcium	19·5	19·5	29·4	29·5
Titanium	23·5	23·3	35·3	35·2
Peroxide	15·3	15·5		
Weight loss	34·1	34·0		
	$Ca_3Ti_2O_5(O_2)_2.4H_2O$		$Ca_3Ti_2O_7$	
Calcium	27·7	27·8	36·8	36·7
Titanium	22·2	22·2	29·3	29·2
Peroxide	14·5	14·8		
Weight loss	24·6	24·1		
	$Ca_4Ti_3O_8(O_2)_2.6H_2O$		$Ca_4Ti_3O_{10}$	
Calcium	26·4	26·5	34·5	34·6
Titanium	23·9	23·8	31·1	31·0
Peroxide	11·0	10·6		
Weight loss	23·6	23·2		
	$CaTi_2O_4(O_2).4H_2O$		'$CaTi_2O_5$'	
Calcium	13·1	13·2	18·5	18·6
Titanium	31·7	31·5	44·5	44·4
Peroxide	10·7	10·5		
Weight loss	29·5	29·0		
	$CaTi_4O_7(O_2)_2.6H_2O$		'$CaTi_4O_9$'	
Calcium	7·9	7·8	10·6	10·7
Titanium	37·3	37·2	51·1	51·0
Peroxide	12·2	12·4		
Weight loss	26·7	27·1		
	$Ca_2TiO_3(O_2).2H_2O$		'Ca_2TiO_4'	
Calcium	33·0	32·9	41·7	41·7
Titanium	19·8	19·6	24·8	24·9
Peroxide	12·8	13·1		
Weight loss	21·9	21·3		

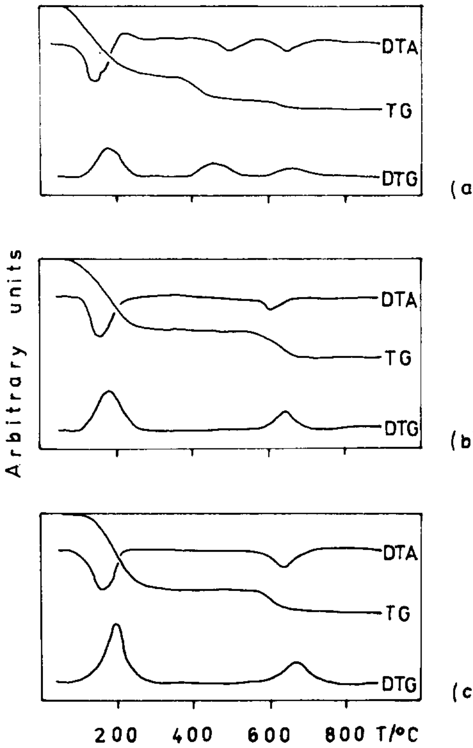

Fig. 1. DTA, TG and DTG curves of (a) $CaTiO_2(O_2).3H_2O$, (b) $Ca_3Ti_2O_5(O_2)_2.4H_2O$ and (c) $Ca_4Ti_3O_8(O_2)_2.6H_2O$.

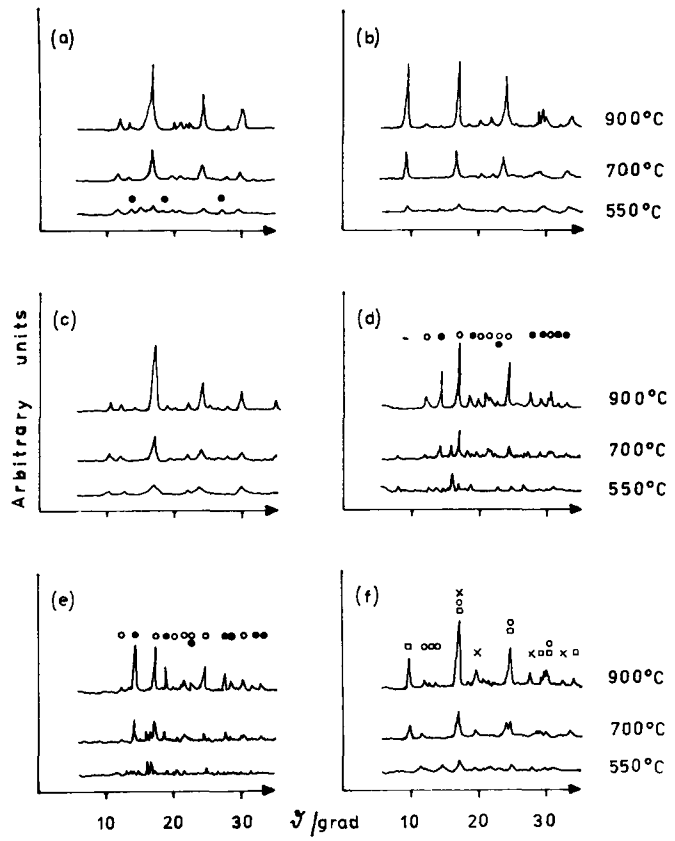

Fig. 2. X-ray diffractograms of the decomposition products of (a) $CaTiO_2(O_2).3H_2O$, (b) $Ca_3Ti_2O_5(O_2)_2.4H_2O$, (c) $Ca_4Ti_3O_8(O_2)_2.6H_2O$, (d) $CaTi_2O_4(O_2).4H_2O$, (e) $CaTi_4O_7(O_2)_2.6H_2O$ and (f) $Ca_2TiO_3(O_2).2H_2O$. Reflections of (●) rutile, (×) CaO, (○) $CaTiO_3$, (□) $Ca_3Ti_2O_7$.

groups occurs between 500 and 750°C and oxygen is released (endothermic effect). $CaTiO_2(O_2).3H_2O$ shows another behaviour. The water liberation occurs in two steps at temperatures of about 150 and 450°C. Oxygen is at first formed between 600 and 700°C.

The X-ray diffractograms of the decomposition products of the three precursors as well as of the dried precipitates of reactions (4), (5) and (6) are shown in Fig. 2 for the calcination temperatures 550, 700 and 900°C (in each case calcined for 8 h). All precipitates and the powders obtained after heating up to 500°C are X-ray amorphous. There are no reflections in the diffractograms, presumably because of the very small crystallite sizes. At 550°C, small reflections appear, indicating the formation of titanate phases or rutile. The last one is found after decomposition of $CaTiO_2(O_2).3H_2O$ and of the precursors of reactions (4) and (5) besides $CaTiO_3$. On the other hand, CaO is one of the products formed above 550°C in the case of the degradation of $Ca_2TiO_3(O_2).2H_2O$. The compounds $CaTiO_3$, $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$ are obtained in their pure form upon calcination at 900°C for 1 h. The specific surface areas of these titanates attain values of $18\,m^2/g$ ($CaTiO_3$), $19\,m^2/g$ ($Ca_3Ti_2O_7$) and $20\,m^2/g$ ($Ca_4Ti_3O_{10}$).

The results of the sintering experiments at 1200 and 1400°C are shown in Figs 3 and 4. The different green densities ρ_o of the compacts ($2{\cdot}35\,g/cm^3$ for $CaTiO_3$, $2{\cdot}06\,g/cm^3$ for $Ca_3Ti_2O_7$, $2{\cdot}13\,g/cm^3$ for $Ca_4Ti_3O_{10}$) are included by using the densification parameter $\alpha = \rho_t - \rho_o/\rho_{th} - \rho_o$ (ρ_t = density at a given time. ρ_{th} = theoretical density). Isothermal sintering at 1200 and 1400°C leads to a good densification in all cases, increasing in the sequence $Ca_3Ti_2O_7 < Ca_4Ti_3O_{10} < CaTiO_3$. The highest densities after 4 h at 1400°C are $3{\cdot}97\,g/cm^3$ for $CaTiO_3$ (98% of ρ_{th}), $3{\cdot}48\,g/cm^3$ for $Ca_3Ti_2O_7$ (91%) and $3{\cdot}84\,g/cm^3$ for $Ca_4Ti_3O_{10}$ (92%). $CaTiO_3$ has a significantly higher sinterability than the other two titanates.

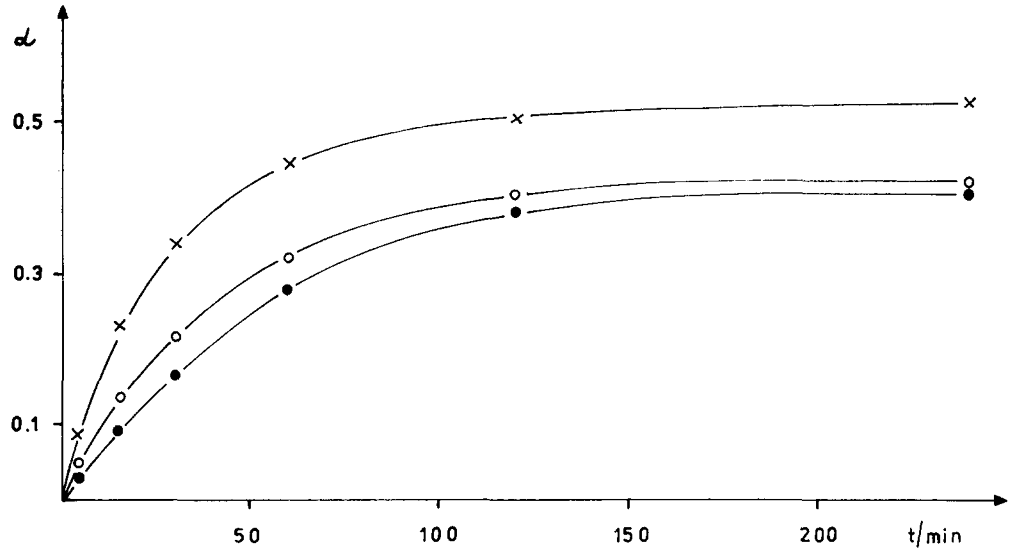

Fig. 3. Densification parameter of (×) $CaTiO_3$, (●) $Ca_3Ti_2O_7$ and (○) $Ca_4Ti_3O_{10}$ compacts as a function of isothermal heating time at 1200°C.

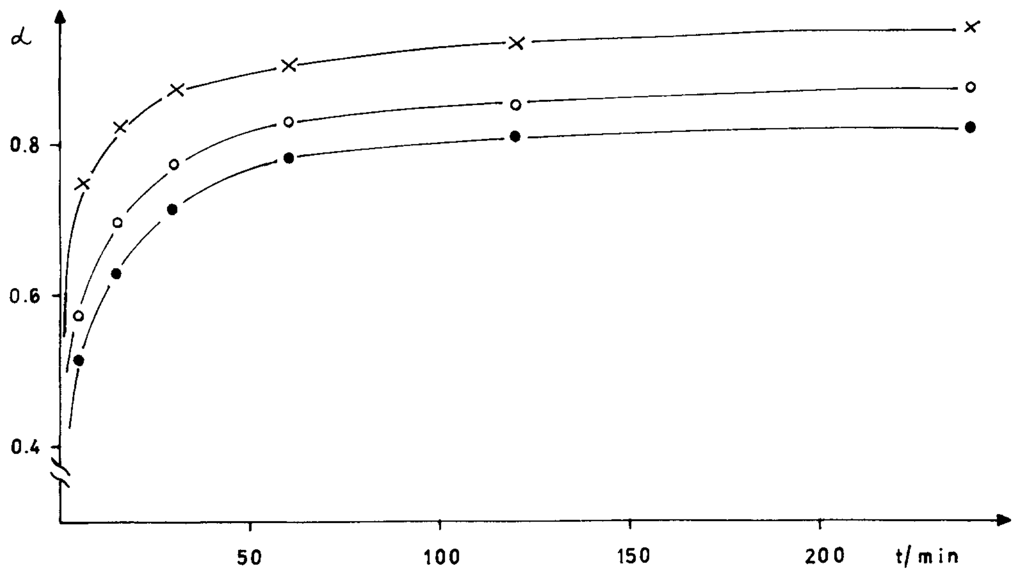

Fig. 4. Densification parameter of (×) $CaTiO_3$, (●) $Ca_3Ti_2O_7$ and (○) $Ca_4Ti_3O_{10}$ compacts as a function of isothermal heating time at 1400°C.

4 Discussion

$CaTiO_3$ has already been synthesized using the peroxide route.[21] It is possible to obtain a series of new precursors by this method by choosing suitable molar ratios of $CaCl_2 . 6H_2O$, $TiCl_4$, H_2O_2 and NH_3. Their compositions are $Ca_3Ti_2O_5(O_2)_2 . 4H_2O$, $Ca_4Ti_3O_8(O_2)_2 . 6H_2O$, $CaTi_2O_4(O_2) . 4H_2O$, $CaTi_4O_7(O_2)_2 . 6H_2O$ and $Ca_2TiO_3(O_2) . 2H_2O$. These precursors are transformed into the corresponding titanates by thermal decomposition in the cases of $Ca_3Ti_2O_5(O_2)_2 . 4H_2O$ and $Ca_4Ti_3O_8(O_2)_2 . 6H_2O$. The resulting calcium titanates $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$ have good stoichiometry and also high purity (main impurities, determined by atom emission spectrometry: Al 90 ppm, Si 40 ppm, Fe 10 ppm, Mn 20 ppm, Mg 30 ppm).

Thermal degradation of the other three precursors at temperatures up to 900°C leads to mixtures of $CaTiO_3$ and TiO_2 in the molar ratios 1:1 for $CaTi_2O_4(O_2) . 4H_2O$ and 1:3 for $CaTi_4O_7(O_2) . 4H_2O$ or to a mixture of $CaTiO_3$, $Ca_3Ti_2O_7$ and CaO for $Ca_2TiO_3(O_2) . 2H_2O$. The specific surface areas of $CaTiO_3$, $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$ obtained after the degradation of the corresponding precursors at 900°C for 1 h attain values of about 19 m^2/g. Scanning electron micrographs show particle sizes between 50 and 150 nm with a high degree of agglomeration. The last statement is supported by sedimentation measurements yielding $d_{50\%}$-values between 500 and 1000 nm. The powders have interesting chemical and morphologic properties in comparison with the same compositions obtained by the solid-state reaction. Their impurity content is normally lower, the keeping of stoichiometry is less problematic and the particles are essentially smaller than in the case of the conventionally prepared powders.

The thermal decomposition of the peroxo-precursors $Ca_3Ti_2O_5(O_2)_2 . 4H_2O$ and $Ca_4Ti_3O_8(O_2)_2 . 6H_2O$ takes place in two steps. The water evaporation, as the first step, is followed by oxygen liberation at higher temperatures, in accord with the situation for the analogous strontium compounds.[27] The degradation of $CaTiO_2(O_2) . 3H_2O$ is a three-step process where the water evaporates in two steps and the oxygen is liberated finally. The X-ray diffractograms show the occurrence of rutile as an intermediate compound at temperatures between 550 and 650°C. A similar mechanism of decomposition has been found for $BaTiO_2(O_2) . 3H_2O$ and $SrTiO_2(O_2) . 3H_2O$.[21,24] In analogy to the corresponding strontium compounds, the precursors $Ca_3Ti_2O_5(O_2)_2 . 4H_2O$ and $Ca_4Ti_3O_8(O_2)_2 . 6H_2O$ are transformed directly to $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$ by the thermal degradation.

Another situation has been observed for the peroxo-precursors $CaTi_2O_4(O_2) . 4H_2O$ and $CaTi_4O_7(O_2)_2 . 6H_2O$. After thermal treatment of $CaTi_4O_7(O_2)_2 . 6H_2O$ at 550°C, a diffractogram is obtained containing all reflections of $CaTi_4O_9$ described in the literature.[8] The intensities of the reflections are low at this temperature, but the interpretation is unambiguous. At 700°C, a mixture of $CaTi_4O_9$, $CaTiO_3$ and rutile is found in the diffractogram, indicating that $CaTi_4O_9$ is only stable at temperatures lower than 700°C. The decomposition of $CaTi_2O_4(O_2) . 4H_2O$ at 550°C leads to a diffractogram containing patterns which have been described for $CaTi_2O_5$,[7] but there are also patterns for which the indication by known phases is not possible. Not all reflections declared for $CaTi_2O_5$ have been found.

At 700°C, a mixture of this phase together with $CaTiO_3$ and rutile is detectable, and at 900°C, the diffractogram contains only the patterns of $CaTiO_3$ and TiO_2. These two phases are stable even at temperatures up to 1400°C. The same situation has been found for the decomposition of $CaTi_4O_7(O_2)_2 . 6H_2O$ at temperatures higher than 700°C. A quantitative valuation of the two diffractograms obtained after thermal treatment of $CaTi_2O_4(O_2) . 4H_2O$ and $CaTi_4O_7(O_2)_2 . 6H_2O$ at 900°C shows the decreasing ratio $CaTiO_3$:TiO_2 which is 1:1 in the first case and 1:3 in the last case.

The decomposition of the precursor $Ca_2TiO_3(O_2) . 2H_2O$ takes place in this way, so that $CaTiO_3$, $Ca_3Ti_2O_7$ and CaO are formed. At 550°C, mainly $CaTiO_3$ reflections are found in the diffractogram, but with rising temperature the patterns of $Ca_3Ti_2O_7$ and CaO increase. There are no indications of the existence of Ca_2TiO_4, confirming the calculations to the stability of this phase.[6]

The sintering behaviour of the titanates $CaTiO_3$, $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$ is similar to that of the corresponding strontium compositions.[27] $CaTiO_3$, with its perovskite structure, shows the best densification at 1200 and 1400°C. The rate of densification decreases in the sequence $CaTiO_3 > Ca_4Ti_3O_{10} > Ca_3Ti_2O_7$. There should be a close connection with the crystal structure of these titanates, higher sinterability being found for higher fractions of perovskite-like layers in the stacking frequency.

5 Conclusions

$CaTiO_3$, $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$ can be synthesized with high purity using the peroxide route. The titanate powders show large specific surface areas and small grain sizes, leading to a high sinterability, which increases in the sequence $Ca_3Ti_2O_7 < Ca_4Ti_3O_{10} < CaTiO_3$. Peroxo-precursors of different composition are formed during the synthesis by a precipitation step from aqueous solutions. The precursors are X-ray amorphous but show definite stoichiometries. Their thermal decomposition leads directly to the titanates for the cases of $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$. Rutile occurs as an intermediate during the formation of $CaTiO_3$ starting from the precursor $CaTiO_2(O_2) . 3H_2O$. Experiments to obtain the titanates $CaTi_2O_5$, $CaTi_4O_9$ and Ca_2TiO_4 lead to different results, stoichiometric precursors are also formed, but the thermal degradation at higher temperatures yields mixtures of $CaTiO_3$ and rutile in the first two cases and of $CaTiO_3$, $Ca_3Ti_2O_7$ and CaO in the last case. $CaTi_4O_9$ is formed below 700°C. There are also indications of the existence of $CaTi_2O_5$ below this temperature. Ca_2TiO_4 cannot be synthesized using the peroxide route, agreeing with the known thermodynamic calculations.

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