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Synthesis of Calcium Titanate Powders by the Sol-Gel Process

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Crystalline, phase-pure, submicrometer-sized calcium titanates have been produced by a sol-gel method at low temperatures. Chemical reaction between calcium acetate and titanium(IV) isopropoxide leads to the formation of optically transparent homogeneous calcium titanate gels. After suitable drying and calcination treatments, the calcium titanate gels are converted to calcium titanate powders. $CaTiO_3$, $Ca_3Ti_2O_7$, and $Ca_4Ti_3O_{10}$ can be synthesized by this way as very sinter-active materials. The rate of densification during the sintering of compacts increases as $Ca_3Ti_2O_7 < Ca_4Ti_3O_{10} < CaTiO_3$. The phases $CaTi_2O_5$ and $CaTi_4O_9$ can be formed as intermediates during the thermal degradation of the corresponding gel precursors at temperatures below 700 °C. They are metastable and decompose to $CaTiO_3$ and rutile during the further thermal treatment. The calcium titanate gels and the titanate powders were characterized by DTA, TG, XRD, SEM, B.E.T. measurements and chemical analysis.

Introduction

Calcium titanates are interesting compounds, in particular with regard to their electrical properties. The phase equilibria in the $CaO-TiO_2$ system have been studied extensively, and the existence of the stable phases $CaTiO_3$, $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$ has been reported in the literature.[1-5] The phase diagram of Jongejan and Wilkins[5] is shown in Figure 1. It has been shown that the composition Ca_2TiO_4 is thermodynamically unstable toward decomposition to other phases.[6] There are also some investigations on the synthesis of $CaTi_2O_5$ and $CaTi_4O_9$ using wet chemical routes.[7-9] These compositions are described to be formed below 800 °C by calcination of calcium- and titanium-containing precursors.

$CaTiO_3$, with its perovskite structure, is an n-type semiconductor on annealing at high temperatures under reducing atmospheres or by donor doping.[10-12] 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]

Calcium titanates are normally synthesized by solid-state reaction between $CaCO_3$ 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, and it has been found that open porosity decreases with increasing sintering temperature, reaching 5% at 1600 °C, when the most reactive starting compounds were used.[13,14] $CaTiO_3$ can also be prepared by wet chemical processes. Its formation is possible by thermal decomposition of precipitated calcium titanyl oxalate[15,16] or by heating of a catecholate complex at 600 °C.[17] Fine $CaTiO_3$ powders consisting of 0.1-0.5-μm 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.[18] The so-obtained powders are sinterable to high-density ceramics below 1400 °C. Homogeneous $CaTiO_3$ can also

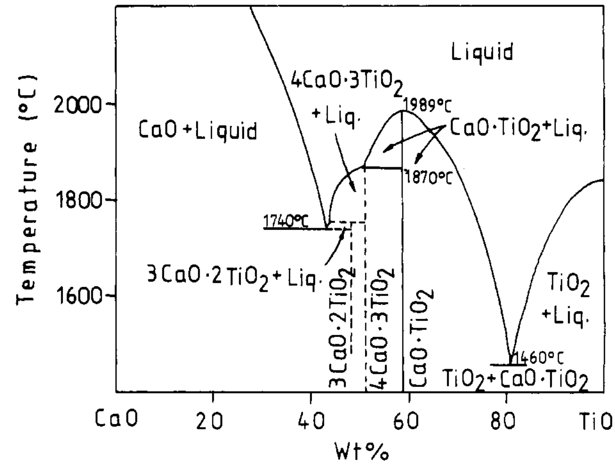

Figure 1. $CaO-TiO_2$ phase diagram obtained by Jongejan and Wilkins.[5]

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be synthesized by a modified Pechini method.[10,19] Another method for the preparation of $CaTiO_3$, $Ca_3Ti_2O_7$, and $Ca_4Ti_3O_{10}$ is the peroxide route via peroxo precursors of definite stoichiometry using $CaCl_2$, $TiCl_4$, H_2O_2, and NH_3 as starting compounds.[9,20] The preparation is likewise possible by the use of titanium(IV) isopropoxide instead of $TiCl_4$.[21] Sintered densities as high as 98% of theoretical were obtained for the so-prepared calcium titanate powders.[9] The phases $CaTi_2O_5$ and $CaTi_4O_9$ can be synthesized after thermal degradation of corresponding peroxo precursors at temperatures below 700 °C.[9]

The primary objective of the present paper was the synthesis of calcium titanates of various compositions via a sol–gel method. The here described route has already been used for the preparation of various barium titanate and strontium titanate powders.[22,23] Calcium acetate and titanium(IV) isopropoxide were not used as the starting compounds to obtain high-purity, homogeneous, stoichiometric, and ultrafine calcium titanate powders. The preparation of the gel precursors, their thermal degradation 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 here.

Experimental Section

In a 500-mL round-bottom flask 16.8 g of CaO (E. Merck, Darmstadt) was dissolved in 30 mL of concentrated acetic acid. Methanol (50 mL) was added to this solution. The resultant mixture was added slowly to a solution of 85.17 g of titanium(IV) isopropoxide (E. Merck, Darmstadt) in the same volume of dried *n*-butanol at 25 °C while stirring (Ca:Ti = 1:1). Four other reaction mixtures were prepared in a similar manner; however, using the Ca:Ti ratios of 3:2, 4:3, 1:2, and 1:4. The calculated amount of water for the hydrolysis reaction was then added to the solutions. The following slowly evaporation lead to optically transparent homogeneous gels. White gel powders were obtained by drying the gels at 110 °C in air. The gel powders were calcined in air at temperatures up to 900 °C. Thermogravimetric analysis (TG, Thermogravimetric Analyzer 951, duPont Instruments), differential thermal analysis (DTA, Thermal Analyst System 2100, duPont Instruments), X-ray diffraction (XRD, CuKα radiation, Philips PW 1710), scanning electron microscopy (SEM, JEOL, JSM 6300F), and chemical analysis (Ti as TiO_2 after precipitation with cupferron and annealing, Ca by complexometric titration with thymolphthalexon as indicator).

The impurity content of certain elements was measured using atomic absorption spectrometry (AAS; Perkin-Elmer, 303) or atomic emission spectrometry (AES, PGS2, Carl Zeiss Jena). Surface characterization of the calcium titanate powders was carried out by B.E.T. measurements (Accusorb 2100 D, Micromeritics, nitrogen adsorption).

Three calcium titanate powders obtained by calcining the gels at 900 °C for 1 h were investigated with respect to their sintering behavior. The powders were mixed with a binder solution (65% H_2O, 25% glycerol, 10% PVA) in a mortar, deagglomerated for 20 min in a ball mill, dried, and sieved out at 80 mesh. The powders were pressed in the form of disks under a pressure of 125 MPa and sintered at 1200 and 1400 °C. The densities of the specimens were determined by weighing and by measuring dimensions using a micrometer before and after each heating step.

Results

The synthesis described above results in optically transparent homogeneous gels which on thermal treatment to temperatures above 500 °C lead to crystalline materials. Table 1 gives the results of the analysis of the powders obtained after calcination of the dried gel precursors at 900 °C. The values for the calcium and titanium contents of the five titanate powders are very close to the expected compositions. A similar situation has been observed for some barium titanates and strontium titanates prepared by this route.[22,23]

Table 1. Analytical Data of the Calcium Titanate Powders Obtained after Thermal Decomposition of the Dried Gel Precursors at 900 °C for 1 h

	Ca content (wt %)		Ti content (wt %)		
	exptl	calc	exptl	calc	Ca:Ti
$CaTiO_3$	29.4	29.5	35.3	35.2	1.00
$Ca_3Ti_2O_7$	36.6	36.7	29.3	29.2	1.49
$Ca_4Ti_3O_{10}$	34.4	34.6	31.1	31.0	1.32
"$CaTi_2O_5$"	18.4	18.6	44.5	44.4	0.49
"$CaTi_4O_9$"	10.6	10.7	51.1	51.0	0.25

Table 2. Surface Area and Analytical Data of Calcium Titanate Powders Obtained after Thermal Treatment of the Dried Gel Precursors at 900 °C for 1 h

	specific surface area ($m^2 g^{-1}$)	d_{BET} (μm)	d_{ELMI} (μm)	impurities (ppm)				
				Al	Ba	Na	Si	Sr
$CaTiO_3$	21	0.07	0.1	80	60	50	50	70
$Ca_3Ti_2O_7$	24	0.07	0.1	60	60	60	50	50
$Ca_4Ti_3O_{10}$	23	0.06	0.1	60	50	50	60	40

The formation of the calcium titanate gels is probably attributed to the modification of the titanium(IV) isopropoxide to species of the type $Ti(OPr)_x(OAc)_y$ where x and y depend upon the Ac:Ti ratio. Six-coordinated titanium is formed during this reaction step. The addition of water causes hydrolysis of the alkoxy and of the acetate groups with a faster rate of hydrolysis for the alkoxy groups.[24] The gel formation can be seen as an association of TiO_6 octahedra by the hydrolysis with localization of Ca^{2+} ions in pores of the gel. The crystallization of the calcium titanates probably occurs as a result of a direct reaction between Ca^{2+} and associated stabilized titanium species. The varying Ca/Ti ratios of the reactions lead to certain differences in the gelation behavior. So the gels show a higher viscosity with decreasing Ca/Ti ratio. On the other hand, no differences in the rate of crystallization of these gels during thermal treatment can be observed by X-ray diffraction.

Table 2 contains surface data and further analytical values for the calcium titanates $CaTiO_3$, $Ca_3Ti_2O_7$, and $Ca_4Ti_3O_{10}$. Large specific surface areas resulting from very small particles are characteristic for the titanates. The high surface energies effect a strong agglomeration which is evident in the electron micrographs. Figure 2 shows the electron micrographs of the gel precursor for $CaTiO_3$ and of its decomposition products at 550 and 900 °C. It seems that the sintering process is already starting at temperatures below 550 °C. $CaTiO_3$ obtained after calcination at 900 °C shows a strong grain growth owing to sintering of small particles. The results of the impurity analysis show that there are only small amounts of other components like Al, Ba, Na, Si, or Sr in the calcium titanate powders. Carbonate was not detected in any case. The purity of the sol–gel-derived calcium titanate powders is better than that of powders with the same composition prepared by the solid-state reaction between $CaCO_3$ and TiO_2.

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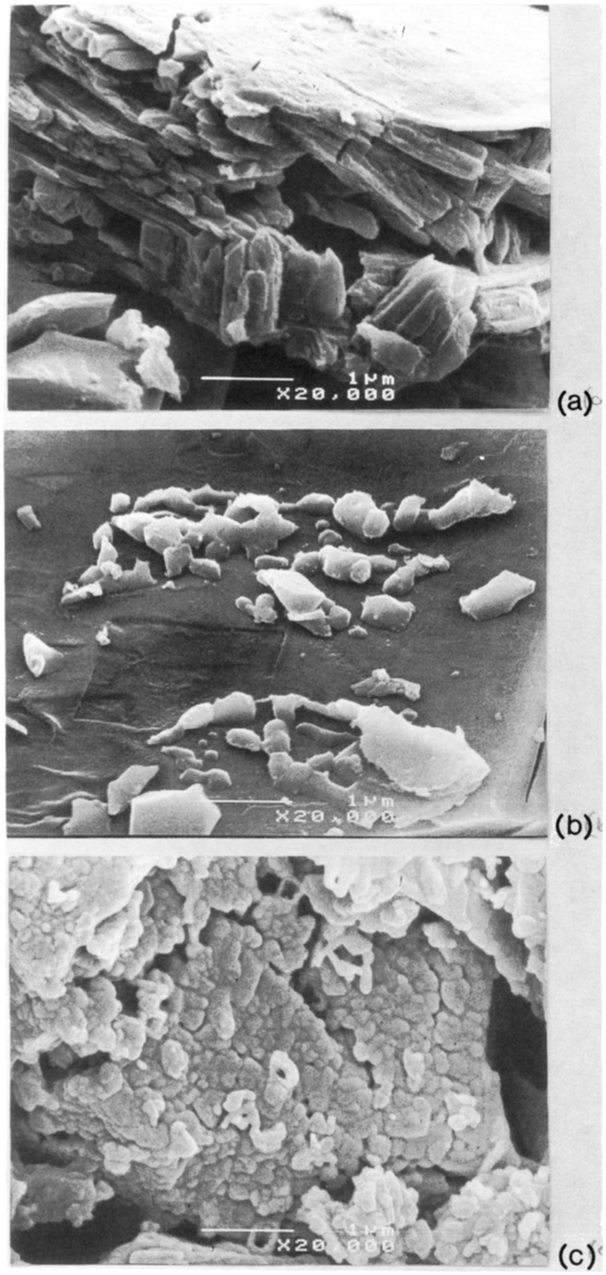

Figure 2. SEM micrographs of (a) the dried gel precursor for $CaTiO_3$, (b) the powder obtained after calcination of the gel precursor at 550 °C for 1 h, and (c) $CaTiO_3$ obtained after calcination of the gel precursor at 900 °C for 1 h.

The TG, DTG, and DTA curves of the five oven-dried gel powders are presented in Figure 3. The gel powders show an initial weight loss below 200 °C resulting from the evaporation of alcohol and desorption of adsorbed moisture. The second weight loss that occurs in the temperature range 300–400 °C can be attributed to the pyrolysis of organic compounds like acetic acid, isopropyl acetate, alcohols, or species formed during the hydrolysis reaction and the gelation process. On heating to 600 °C, the gels undergo an additional weight loss which can be attributed to the remove of the residual organics. The total weight loss amounts to 50–60% for the five gel precursors. Endothermic effects in the DTA curves are indications of these processes. An exotherm above 750 °C observed in all cases is attributed to the crystallization of the gels. The white color of the products obtained after thermal treatment above 750 °C is an indication of the departure of the organics. The continuation of the thermal decomposition of the gels is accompanied by a decrease of the specific surface area of the powders. Table 3 shows the results of B.E.T. measurements including the calculated mean particle sizes for the powders formed during the thermal degradation of the gel precursor for $CaTiO_3$.

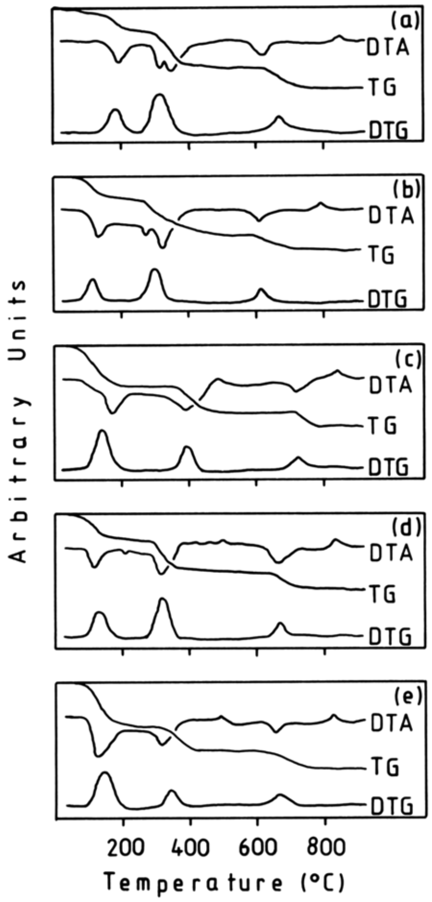

Figure 3. DTA, TG, and DTG curves of the five oven-dried gel precursors for (a) $CaTiO_3$, (b) $Ca_3Ti_2O_7$, (c) $Ca_4Ti_3O_{10}$, (d) "$CaTi_2O_5$", and (e) "$CaTi_4O_9$".

Table 3. Specific Surface Area and Mean Particle Diameter Dependence on the Calcination Conditions for the Powders Obtained during $CaTiO_3$ Format

conditions (h/°C)	specific surface area ($m^2\,g^{-1}$)	mean particle diam (μm)
8/200	145	0.01
8/400	116	0.01
8/600	65	0.02
8/800	29	0.05
8/900	18	0.08

The XRD patterns of the five dried and heat-treated gel powders are shown in Figure 4. The dried gel powders prepared by the described technique and the powders obtained after heating to 450 °C are X-ray amorphous. There are no informations up to now on the influence of other starting compounds such as calcium alkoxides, calcium hydroxide, or other titanium alkoxides on the degree of crystallization of the gels. It is known that sol–gel-derived $BaTiO_3$ shows a high crystallinity already after drying if barium alkoxides are used instead of barium acetate.[25,26] Such results suggest that the structure of the titanate gel powders is dependent on the mechanism of

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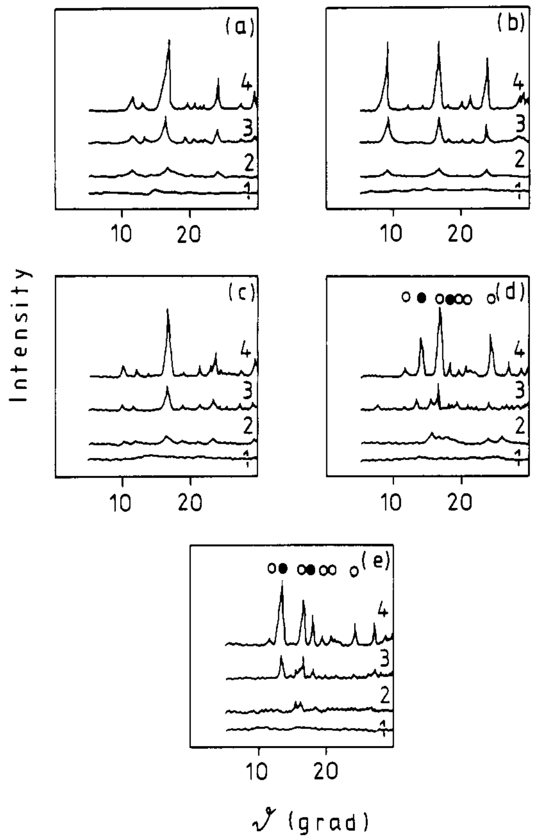

Figure 4. X-ray diffractograms of the oven-dried gel precursors and of the decomposition products obtained during formation of (a) $CaTiO_3$, (b) $Ca_3Ti_2O_7$, (c) $Ca_4Ti_3O_{10}$, (d) "$CaTi_2O_5$", and (e) "$CaTi_4O_9$" (○, $CaTiO_3$; ●, rutile; 1, oven dried, 2, 500 °C; 3, 700 °C; 4, 900 °C, calcination time at each temperature 8 h).

the hydrolysis and polycondensation reactions which is different on the mechanism of the hydrolysis and polycondensation reactions which is different by varying the starting compounds.

Thermal treatment of the gel powders at 500 °C leads to small broad reflections in the X-ray diffractograms indicating the formation of titanate phases. Forced crystallization can be observed by further increasing of the temperature. All essential titanate reflections can be found in the X-ray diffractograms for the products calcined at 700 °C. There is no evidence for intermediate products during the thermal decomposition of the gel precursors for $CaTiO_3$, $Ca_3Ti_2O_7$, and $Ca_4Ti_3O_{10}$ from the XRD patterns. These three titanates are obtained in their pure form upon calcination at 900 °C for 1 h. Another situation has been observed for the degradation of the gel precursors for $CaTi_2O_5$ and $CaTi_4O_9$. After thermal treatment at temperatures of about 500–700 °C, diffractograms are obtained containing most of the reflections of $CaTi_2O_5$ or $CaTi_4O_9$ described in the literature.[7,8] The intensities of the reflections are low at these temperatures, but the interpretation is unambiguous. At 700 °C, mixtures of $CaTi_2O_5$ or $CaTi_4O_9$ together with $CaTiO_3$ and rutile are found in the diffractograms, indicating that $CaTi_2O_5$ and $CaTi_4O_9$ are stable only at temperatures lower than 700 °C. Further calcination above 700 °C leads to mixtures of $CaTiO_3$ and rutile without presence of other titanate phases. $CaTiO_3$ and rutile are stable even at temperatures up to 1400 °C. A quantitative valuation of the two diffractograms obtained after thermal treatment of the gel precursors for $CaTi_2O_5$ and $CaTi_4O_9$ 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. An analogous situation has been found for the preparation of $CaTi_2O_5$ and $CaTi_4O_9$ using the peroxide route.[9] The decomposition of the peroxo precursors $CaTi_2O_4(O_2){\cdot}4H_2O$ and $CaTi_4O_7(O_2)_2{\cdot}6H_2O$ takes place via the phases $CaTi_2O_5$ or $CaTi_4O_9$, too. Thermal treatment at temperatures higher than 700 °C leads likewise to the formation of $CaTiO_3$ and rutile. The formation of $CaTi_2O_5$ and $CaTi_4O_9$ from the amorphous phase at so relatively low temperatures is remarkable. Obviously, these two titanates can be obtained only as metastable compounds at temperatures between 500 and 700 °C using wet chemical methods such as the here-desribed sol–gel process or the peroxide route.

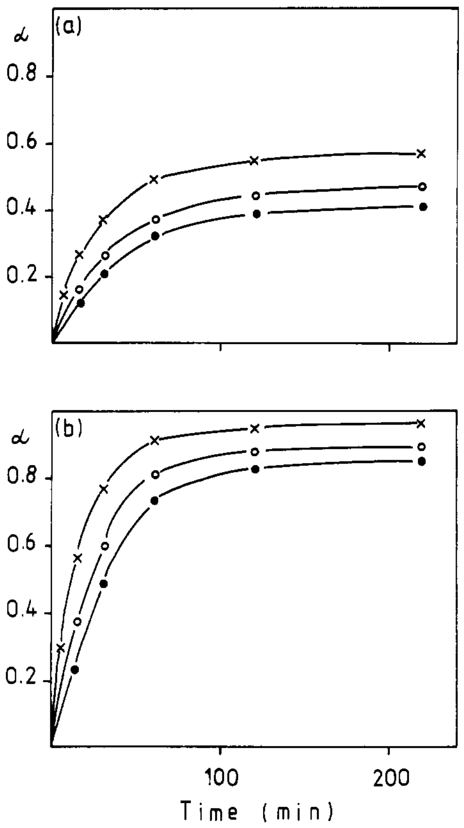

Figure 5. Densification parameter of $CaTiO_3$ (×), $Ca_3Ti_2O_7$ (○), and $Ca_4Ti_3O_{10}$ (●) compacts as a function of isothermal heating time at (a) 1200 and (b) 1400 °C.

The results of sintering experiments at 1200 and 1400 °C are presented in Figure 5. The different green densities, ρ_0, of the compacts (2.45 g cm^{-3} for $CaTiO_3$, 2.16 g cm^{-3} for $Ca_3Ti_2O_7$, 2.22 g cm^{-3} for $Ca_4Ti_3O_{10}$) are included by using the densification parameter $\alpha = (\rho_t - \rho_0)/(\rho_{th} - \rho_0)$ (ρ_t = density at a given time, ρ_{th} = theoretical density). Isothermal sintering at 1200 °C leads to a strong densification for the three titanates, increasing in the order $Ca_3Ti_2O_7 < Ca_4Ti_3O_{10} < CaTiO_3$. The highest densities after 4 h at 1200 °C are 3.36 g cm^{-3} for $CaTiO_3$ (83% of ρ_{th}), 2.94 g cm^{-3} for $Ca_3Ti_2O_7$ (77%), and 3.02 g cm^{-3} for $Ca_4Ti_3O_{10}$ (72%). Sintering at 1400 °C leads to a very strong shrinkage of the samples with density values near to the theoretical density after 4 h. The order of the densities is the same as in the case of sintering at 1200 °C. The highest reached densities at 1400 °C are 4.00 g cm^{-3} for $CaTiO_3$ (99%), 3.65 g cm^{-3} for $Ca_3Ti_2O_7$ (96%), and 3.88 g cm^{-3} for $Ca_4Ti_3O_{10}$ (93%). The comparison of the sintering results of the here-discussed sol–gel-derived powders with those of calcium titanates obtained by the peroxide route shows similar sinterabilities for both cases with a little better densification for the substances prepared by the sol–gel process. The comparison with the sintering results of calcium titanates obtained by the solid-state reaction at temperatures of ca. 1350 °C shows a significantly better sinterability for $CaTiO_3$, $Ca_3Ti_2O_7$, and $Ca_4Ti_3O_{10}$ formed by the sol–gel method or by the peroxide route. The described sol–gel technique can be used also for the synthesis of complex calcium-, strontium-, and barium-containing titanates. The interesting properties of these titanates allow the preparation of electroceramic elements at lower temperatures than in the case of using titanates obtained by the traditionally mixed-oxide route.

Conclusions

A sol–gel method has been developed here to prepare calcium titanate powders of various compositions. Transparent gels result from reactions of calcium acetate and titanium(IV) isopropoxide in alcoholic solutions. Thermal treatment of the amorphous gels to temperatures of 900 °C leads to single phase crystalline titanates in the case of $CaTiO_3$, $Ca_3Ti_2O_7$, and $Ca_4Ti_3O_{10}$ at lower temperatures than traditional high-temperature solid-state materials. The thermal decomposition of the gel precursors leads directly to the corresponding titanates in these cases. The resulting ultrafine powders have a small impurity content. They show a high sinterability at temperatures above 1000 °C which increases in the order $Ca_3Ti_2O_7 < Ca_4Ti_3O_{10} < CaTiO_3$. Experiments to obtain the titanates $CaTi_2O_5$ and $CaTi_4O_9$ lead to the formation of these two phases during the thermal degradation of the corresponding gel precursors as intermediate products at temperatures of about 500–700 °C. It is not possible to get phase-pure materials in these cases. The metastability of $CaTi_2O_5$ and $CaTi_4O_9$ leads to the formation of $CaTiO_3$ and rutile beginning at temperatures lower than 700 °C. The described sol–gel method allows to prepare complex calcium-, strontium-, and barium-containing titanate powders with the desired stoichiometry.