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Peroxide Route to Synthesize Strontium Titanate Powders of Different Composition

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Abstract

The strontium titanates $SrTiO_3$, Sr_2TiO_4, $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ can be synthesized to a good quality by the wet chemical peroxide route. At first, peroxo-precursors of definite stoichiometry are formed during the preparation. These are then transformed into the titanates by thermal decomposition. The resulting strontium titanate powders are of ultrafine nature and have a high purity. They show high sintering activity at temperatures >1200°C. The densification behaviour during sintering is improved in the sequence $Sr_2TiO_4 < Sr_3Ti_2O_7 < Sr_4Ti_3O_{10} < SrTiO_3$.

Die Strontiumtitanate $SrTiO_3$, Sr_2TiO_4, $Sr_3Ti_2O_7$ und $Sr_4Ti_3O_{10}$ können mit der Peroxidmethode auf naßchemischem Weg in guter Qualität synthetisiert werden. Bei der Präparation werden zunächst Peroxo-Precursor definierter Stöchiometrie gebildet, die durch thermische Zersetzung in die Titanate überführbar sind. Die entstehenden Strontiumtitanatpulver sind ultrafein und von großer Reinheit. Sie sind bei Temperaturen >1200°C sehr sinteraktiv. Das Verdichtungsverhalten beim Sintern verbessert sich in der Reihenfolge $Sr_2TiO_4 < Sr_3Ti_2O_7 < Sr_4Ti_3O_{10} < SrTiO_3$.

Par chimie humide, voie peroxyde, on synthétise des poudres de titanates de strontium $SrTiO_3$, Sr_2TiO_4, $Sr_3Ti_2O_7$ et $Sr_4Ti_3O_{10}$, de bonne qualité. On forme pendant la préparation des précurseurs peroxydes à stoechiométrie définie, qui sont ensuite transformés en titanates par décomposition thermique. Les poudres de titanate de strontium ainsi fabriquées sont ultrafines et très pures. Elles sont très réactives au frittage aux températures >1200°C. Le comportement à la densification pendant le frittage est amélioré suivant la séquence $Sr_2TiO_4 < Sr_3Ti_2O_7 < Sr_4Ti_3O_{10} < SrTiO_3$.

1 Introduction

Strontium titanates are important solids because of their interesting electrical properties. A number of studies of phase equilibria in the $SrO–TiO_2$ system have shown the existence of the titanate compositions $SrTiO_3$, Sr_2TiO_4, $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$.[1–5] $SrTiO_3$, which has the cubic perovskite structure, is technically the most important compound among these titanates. Non-stoichiometric or doped *n*-type semiconducting $SrTiO_3$ has been studied as a dielectric and photoelectrode material.[6,7] Sr_2TiO_4 is found to be stable in the body-centred tetragonal K_2NiF_4 structure, supporting the idea that $SrTiO_3$ accommodates non-stoichiometry in its structure through the formation of alternating layers of perovskite $SrTiO_3$ and rock salt SrO along the *c*-direction.[2,8] The structure of $Sr_3Ti_2O_7$ also consists of layers along the *c*-direction, two perovskite and then one rock salt, with a body-centred tetragonal cell.[3] $Sr_4Ti_3O_{10}$ is found to exist in a body-centred tetragonal structure which contains three perovskite and then one rock salt layer along the *c*-direction.[3,5] The formation of higher members of the homologous series $SrO \, . \, nSrTiO_3$ with $n > 4$ is discussed in similar terms.[8,9] With the lattice imaging technique, using transmission electron microscopy, intergrowths of the oxides $Sr_4Ti_3O_{10}$, $Sr_5Ti_4O_{13}$, $Sr_6Ti_5O_{16}$, $Sr_8Ti_7O_{22}$ and $Sr_9Ti_8O_{25}$ in a disordered $Sr_3Ti_2O_7$ crystal fragment have been detected.[9] Thermodynamic calculations have offered a theoretical basis for the Ruddlesden–Popper-type superlattice formation in the Sr–Ti–O system, starting from the

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incorporation of small amounts of excess SrO through the creation of Sr_{Ti} defects. These calculations have shown that the energies of formation of the members of the homologous series $SrO.nSrTiO_3$ remain the same for $n > 2$.[8]

Strontium titanates are commonly prepared by the solid-state reaction of $SrCO_3$ with TiO_2 at temperatures above 1000°C.[10,11] Temperatures of about 1400°C are frequently used to obtain the pure phases.[3,5]

$SrTiO_3$ can also be synthesized by wet chemical methods. It is formed by thermal decomposition of precipitated $SrTiO(C_2O_4)_2.4H_2O$[12] or by controlled hydrolysis of strontium titanium carboxylates.[13] The obtained carboxy-hydrosols are autoclaved at 300 to 350°C in water for several hours to yield $SrTiO_3$. Another method for this titanate composition is the peroxide route via the precursor $SrTiO_2(O_2).3H_2O$.[14]

It is the aim of this paper to investigate the formation of further strontium titanate compositions like Sr_2TiO_4, $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ using the peroxide method. In the case of the Ba–Ti–O system, Ba_2TiO_4, $BaTiO_3$, $BaTi_2O_5$ and $BaTi_4O_9$ have been obtained by this route.[15–18] The precipitation of the strontium- and titanium-containing precursors, their thermal decomposition to the titanates and the characterization of both intermediate products and the final powders of Sr_2TiO_4, $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ as well as results from sintering experiments are described here.

2 Experimental procedure

An aqueous solution of $SrCl_2.6H_2O$ 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 $SrCl_2.6H_2O:TiCl_4:H_2O_2:NH_3$ used were 1:1:2·5:12 for $SrTiO_3$, 2:1:5:12 for Sr_2TiO_4, 3:2:7:20 for $Sr_3Ti_2O_7$, and 4:3:10:30 for $Sr_4Ti_3O_{10}$. The conditions for the synthesis of $SrTiO_3$ have already been described in a former paper.[14] Light yellow amorphous precipitates were formed in all cases.

The precipitated substances 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 calcined for 1 h at 900°C was performed as follows. Titanium was determined gravimetrically, after precipitation with cupferron and annealing, as TiO_2, and strontium was titrated complexometrically with thymolphthalexon as indicator. The peroxide content was analysed iodometrically.

Thermal decompositions of the precursors were investigated by thermogravimetry (TG) and differential thermal analysis (DTA). X-Ray diffraction measurements showed the formation of the titanate phases.

The strontium 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 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. The tablets with an initial diameter of 10 mm and height of 5 mm were measured for size after heating steps utilizing an external micrometer.

3 Results

The results of the analysis of the dried precursors and of the white powders obtained after calcination

Table 1. Analytical data for the peroxo-precursors and for the strontium titanates (weight loss for 1 h at 900°C)

Component	*$SrTiO_2(O_2).3H_2O$*		*$SrTiO_3$*	
	(% exp.)	*(% calc.)*	*(% exp.)*	*(% calc.)*
Strontium	34·6	34·6	47·8	47·7
Titanium	19·0	18·9	26·2	26·1
Peroxide	12·4	12·6		
Weight loss	27·5	27·6		
	$Sr_2TiO_3(O_2).2H_2O$		*Sr_2TiO_4*	
	(% exp.)	*(% calc.)*	*(% exp.)*	*(% calc.)*
Strontium	51·5	51·7	60·8	61·0
Titanium	14·2	14·1	16·6	16·7
Peroxide	9·2	9·4		
Weight loss	15·6	15·3		
	$Sr_3Ti_2O_5(O_2)_2.4H_2O$		*$Sr_3Ti_2O_7$*	
	(% exp.)	*(% calc.)*	*(% exp.)*	*(% calc.)*
Strontium	45·6	45·7	55·7	55·8
Titanium	16·8	16·7	20·5	20·4
Peroxide	11·4	11·1		
Weight loss	18·5	18·1		
	$Sr_4Ti_3O_8(O_2)_2.6H_2O$		*$Sr_4Ti_3O_{10}$*	
	(% exp.)	*(% calc.)*	*(% exp.)*	*(% calc.)*
Strontium	44·3	44·1	53·6	53·6
Titanium	18·2	18·1	22·1	22·0
Peroxide	8·3	8·1		
Weight loss	17·9	17·6		

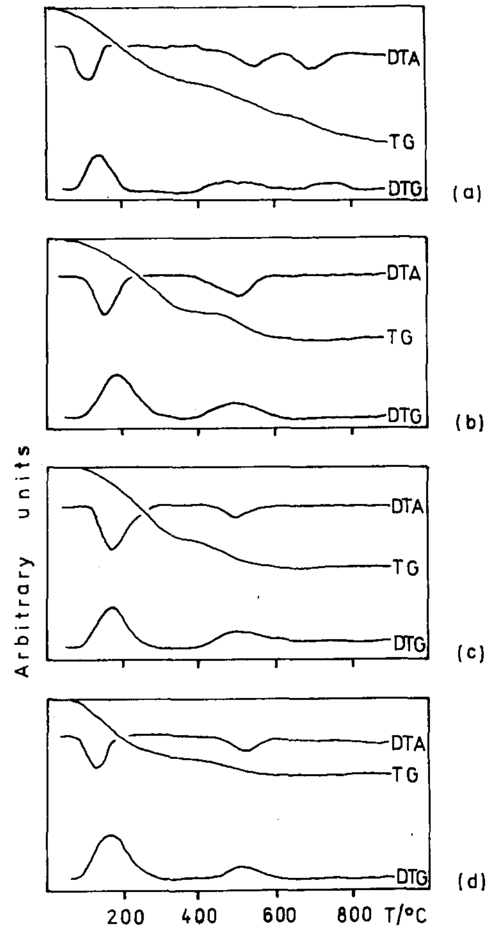

Fig. 1. DTA, TG and DTG curves of (a) $SrTiO_2(O_2).3H_2O$, (b) $Sr_2TiO_3(O_2).2H_2O$, (c) $Sr_3Ti_2O_5(O_2)_2.4H_2O$ and (d) $Sr_4Ti_3O_8(O_2)_2.6H_2O$.

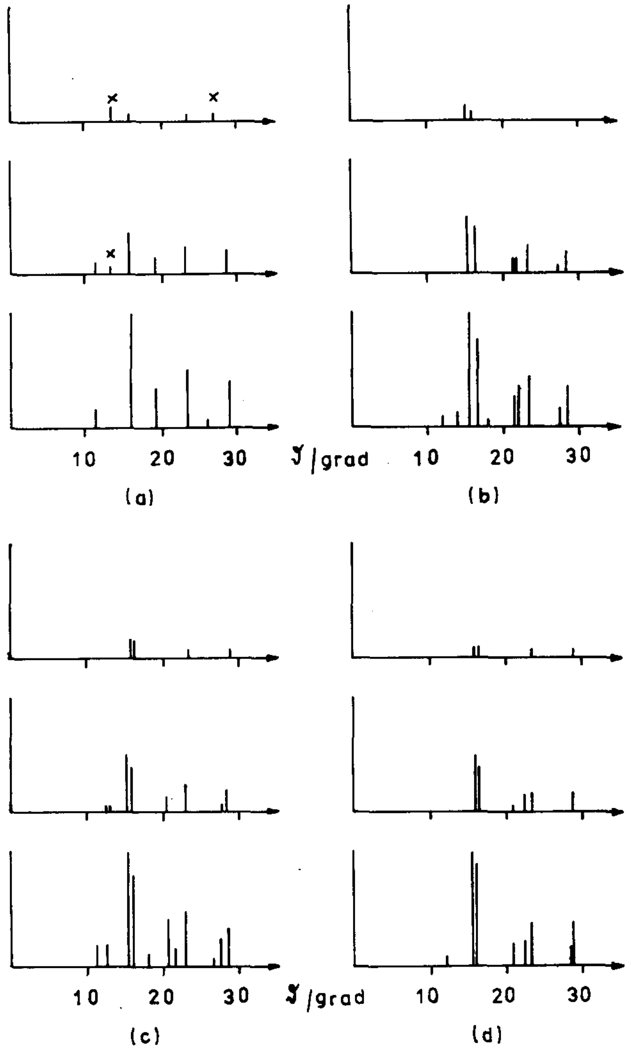

Fig. 2. X-Ray diffraction diagrams of the decomposition products of (a) $SrTiO_2(O_2).3H_2O$, (b) $Sr_2TiO_3(O_2).2H_2O$, (c) $Sr_3Ti_2O_5(O_2)_2.4H_2O$ and (d) $Sr_4Ti_3O_8(O_2)_2.6H_2O$ (× = reflections of rutile).

at 900°C ($SrTiO_3$, Sr_2TiO_4, $Sr_3Ti_2O_7$, $Sr_4Ti_3O_{10}$) are given in Table 1. They show the stoichiometric composition of the peroxo-compounds and of the titanates. The reactions of the precursor formation can be summarized by the following equations:

$$SrCl_2 + TiCl_4 + H_2O_2 + 6NH_3 + 5H_2O \rightarrow SrTiO_2(O_2).3H_2O + 6NH_4Cl \quad (1)$$

$$2SrCl_2 + TiCl_4 + H_2O_2 + 8NH_3 + 5H_2O \rightarrow Sr_2TiO_3(O_2).2H_2O + 8NH_4Cl \quad (2)$$

$$3SrCl_2 + 2TiCl_4 + 2H_2O_2 + 14NH_3 + 9H_2O \rightarrow Sr_3Ti_2O_5(O_2)_2.4H_2O + 14NH_4Cl \quad (3)$$

$$4SrCl_2 + 3TiCl_4 + 4H_2O_2 + 20NH_3 + 12H_2O \rightarrow Sr_4Ti_3O_8(O_2)_2 \cdot 6H_2O + 20NH_4Cl \quad (4)$$

The thermogravimetric, differential thermogravimetric and differential thermal analysis curves of the thermal decomposition of the four precursors are shown in Fig. 1. $Sr_2TiO_3(O_2).2H_2O$, $Sr_3Ti_2O_5(O_2)_2.4H_2O$ and $Sr_4Ti_3O_8(O_2)_2.6H_2O$ show a similar behaviour. The first step up to 300°C corresponds to the evaporation of water (endothermic effect). The peroxide groups decompose between 400 and 600°C and oxygen is released (endothermic effect). Another situation is found for $SrTiO_2(O_2).3H_2O$, where the liberation of water occurs in two steps at temperatures of about 150 and 500°C and oxygen is first formed between 650 and 800°C.

Figure 2 shows the X-ray diffractograms of the decomposition products of the four precursors for three temperatures in each case. The precipitates and the products obtained after heating up to 450°C are amorphous. No reflections can be seen in the diffractograms. At 500°C, small reflections of $SrTiO_3$, Sr_2TiO_4, $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ appear respectively, but there are also very weak patterns of rutile for the case of the decomposition of $SrTiO_2(O_2).3H_2O$. The four titanates are obtained as single phases upon calcination at 900°C. Their specific surface areas reach values of 14 (Sr_2TiO_4), 15 ($SrTiO_3$) and 16 m^2/g ($Sr_3Ti_2O_7$, $Sr_4Ti_3O_{10}$).

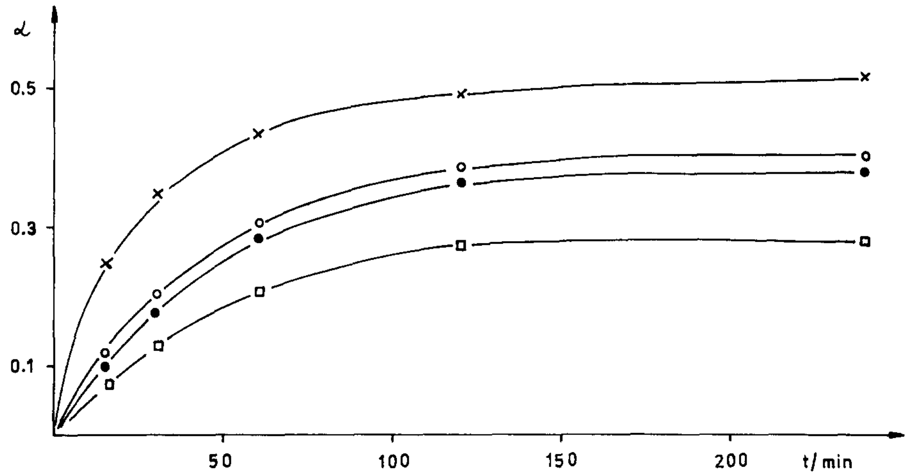

Fig. 3. Densification parameter of (×) $SrTiO_3$, (○) $Sr_4Ti_3O_{10}$, (●) $Sr_3Ti_2O_7$ and (□) Sr_2TiO_4 compacts as a function of isothermal heating time at 1200°C.

The results of the sintering experiments are shown in Fig. 3 (1200°C) and Fig. 4 (1400°C). The different green densities ρ_0 of the compacts (2·61 g/cm^3 for $SrTiO_3$, 2·80 g/cm^3 for Sr_2TiO_4, 2·64 g/cm^3 for $Sr_3Ti_2O_7$, 2·48 g/cm^3 for $Sr_4Ti_3O_{10}$) are included by using the densification parameter $\alpha = \rho_t - \rho_0/\rho_{th} - \rho_0$($\rho_t$ = density at a given time, ρ_{th} = theoretical density—4·74 g/cm^3 for $SrTiO_3$, 5·03 g/cm^3 for Sr_2TiO_4, 5·04 g/cm^3 for $Sr_3Ti_2O_7$, 5·10 g/cm^3 for $Sr_4Ti_3O_{10}$). Good densification can be observed during isothermal sintering at 1200 and 1400°C, increasing in the sequence $Sr_2TiO_4 < Sr_3Ti_2O_7 < Sr_4Ti_3O_{10} < SrTiO_3$. The highest densities after 4 h at 1400°C are 4·60 g/cm^3 for $SrTiO_3$ (97% of ρ_{th}), 4·69 g/cm^3 for $Sr_4Ti_3O_{10}$ (92%), 4·54 g/cm^3 for $Sr_3Ti_2O_7$ (90%) and 4·20 g/cm^3 for Sr_2TiO_4 (83%). The sintering activity of $SrTiO_3$ is significantly higher than that of the other titanates.

4 Discussion

The peroxide route has already been applied to the preparation of $SrTiO_3$.[14] By changing the molar ratios of $SrCl_2 . 6H_2O$, $TiCl_4$, H_2O_2 and NH_3, it is possible to obtain new precursors by precipitation which have the stoichiometric compositions $Sr_2TiO_3(O_2) . 2H_2O$, $Sr_3Ti_2O_5(O_2)_2 . 4H_2O$ and $Sr_4Ti_3O_8(O_2)_2 . 6H_2O$. These precursors can be transformed into the corresponding titanates by thermal decomposition. The resulting strontium titanates Sr_2TiO_4, $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ have good stoichiometry and also high purity (main impurities: Al (80 ppm), Si (40 ppm), Fe (10 ppm), Mn (20 ppm), Mg (20 ppm)). The powders formed after decomposition of the precursors at 900°C for 1 h have relatively large specific surface areas of about 15 m^2/g and particle sizes between 50 and 150 nm with a high degree of agglomeration. This statement is supported by scanning electron micrographs and by sedimentation measurements ($d_{50\%}$ values between 500 and 1000 nm). The powders have interesting chemical and morphological properties in comparison with the same compositions prepared by conventional solid-state reactions. For the latter the impurity content is normally higher, the keeping of stoichiometry is more problematic and the particles are typically larger.

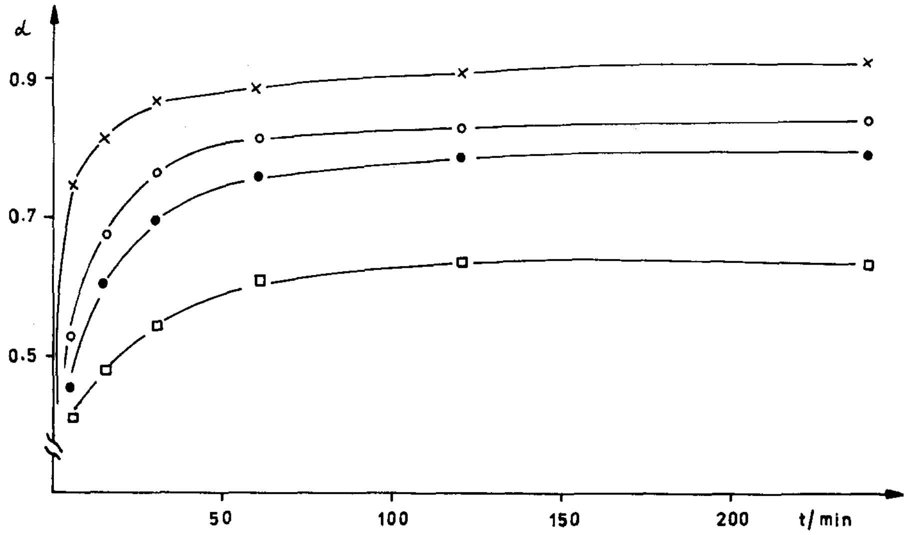

Fig. 4. Densification parameter of (×) $SrTiO_3$, (○) $Sr_4Ti_3O_{10}$, (●) $Sr_3Ti_2O_7$ and (□) Sr_2TiO_4 compacts as a function of isothermal heating time at 1400°C.

Molar ratios of $SrCl_2 . 6H_2O$ and $TiCl_4$ deviating from those used in the described experiments lead after calcination either to $SrTiO_3$ and rutile (in the case of excess Ti) or to a mixture of $SrTiO_3$ and other strontium titanates (in the case of excess Sr).

The thermal decomposition of the peroxo-precursors always shows, in the case of the strontium-rich compositions, a two-step process. In the first step, the water evaporation and in the second step the oxygen liberation take place. In contrast to this behaviour, the water of $SrTiO_2(O_2). 3H_2O$ evaporates in two steps. Rutile can be detected in the X-ray diffratogram as an intermediate compound at temperatures between 550 and 650°C. The mechanism of decomposition is expected to be similar to that which was found for $BaTiO_2(O_2) . 3H_2O$.[16] On the other hand, the precursors $Sr_2TiO_3(O_2) . 2H_2O$, $Sr_3Ti_2O_5(O_2)_2 . 4H_2O$ and $Sr_4Ti_3O_8(O_2)_2 . 6H_2O$ lead, after thermal decomposition, directly to Sr_2TiO_4, $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$. Structural investigations on the X-ray amorphous precursors are at work.

The sintering behaviour of the investigated strontium titanates is dependent on the composition. $SrTiO_3$, with its perovskite structure and the lowest theoretical density, shows the best densification at temperatures above 1200°C. On the other hand, Sr_2TiO_4, with the K_2NiF_4 structure, reaches only a relatively low density after sintering. The sequence of the titanates in regard to sintering activity shows a close connection with the crystal structure, higher activity being found for higher fractions of perovskite-like layers in the stacking sequence.

The phenomenon of X-ray amorphous but stoichiometric precursors has already been found in the case of the Ba compounds.[15–18] The reason presumably lies in a very small crystallite size in the ultrafine powders.

5 Conclusions

The peroxide route can be used successfully for the preparation of $SrTiO_3$, $SrTiO_4$, $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$. The titanate powders show high purity. Their large specific surface areas and small grain sizes lead to high sintering activity which increases in the sequence $Sr_2TiO_4 < Sr_3Ti_2O_7 < Sr_4Ti_3O_{10} < SrTiO_3$. The precipitated peroxo-precursors are X-ray amorphous but show definite stoichiometries. Their thermal decomposition leads directly to the titanates for the cases of Sr_2TiO_4, $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$. In the case of the $SrTiO_3$ preparation, rutile occurs as an intermediate.

References

1. Drys, M. & Trzebiatowski, W., The system strontium oxide–titanium dioxide. *Roczniki Chem.*, **31** (1957) 489–96.
2. Ruddlesden, S. N. & Popper, P., New compounds of the K_2NiF_4 type. *Acta Crystallogr.*, **10** (1957) 538–9.
3. Ruddlesden, S. N. & Popper, P., The compound $Sr_3Ti_2O_7$ and its structure. *Acta Crytallogr.*, **11**(1958) 54–5.
4. Cocco, A. & Massazza, F., Microscopic study of the system SrO–TiO_2. *Ann. Chim.* (*Rome*), **53** (1963) 883–93.
5. McCarthy, G. J., White, W. B. & Roy, R., Phase equilibria in the 1375°C isotherm of the system Sr–Ti–O. *J. Am. Ceram. Soc.*, **52** (1969) 463–7.
6. Burn, I. & Neirmann, S., Dielectric properties of donor-doped polycrystalline strontium titanate (IV). *J. Mater. Sci.*, **17** (1982) 3510–24.
7. Watanabe, T., Fujishima, A. & Honda, K., Photoelectrochemical reactions at a strontium titanate single crystal electrode. *Bull. Chem. Soc. Jpn*, **49** (1976) 355–8.
8. Udayakumar, K. R. & Cormack, A. N., Structural aspects of phase equilibria in the strontium–titanium–oxygen system. *Commun. Am. Ceram. Soc.*, **71** (1988) C469–71.
9. Tilley, R. J. D., An electron microscope study of perovskite-related oxides in the Sr–Ti–O system. *J. Solid State Chem.*, **21** (1977) 293–301.
10. Tagawa, H., Kimura, K., Fujino, T. & Ouchi, K., Reactivity of starting materials in formation of strontium titanate. *Denki Kagaku* (*J. Electrochem. Soc. Jpn*), **52** (1984) 154–9.
11. Tagawa, H. & Igarashi, K., Reaction of strontium carbonate with anatase and rutile. *J. Am. Ceram. Soc.*, **69** (1986) 310–14.
12. Gallagher, P. K., Schrey, F. & DiMarcello, F. V., Preparation of semiconducting titanates by chemical methods. *J. Am. Ceram. Soc.*, **46** (1963) 359–65.
13. Riman, R. E., Landham, R. R. & Bowen, H. K., Synthesis of uniform titanium and 1:1 strontium–titanium carboxyhydrosols by controlled hydrolysis of alkoxymetal carboxylate precursors. *J. Am. Ceram. Soc.*, **72** (1989) 821–6.
14. Pfaff, G., Naßchemische Synthese von $SrTiO_3$- und $CaTiO_3$-Sinterpulvern durch Fällung von $SrTiO_2(O_2) . 3H_2O$ und $CaTiO_2(O_2) . 3H_2O$. *Z. Chem.*, **29** (1989) 30–1.
15. Pfaff, G., Synthesis and characterization of Ba_2TiO_4. *J. Mater. Sci. Lett.*, **10** (1991) 1059–60.
16. Pfaff, G., Herstellung von $BaTiO_3$-Sinterpulver durch Fällung von $BaTiO_2(O_2) . 3H_2O$. *Z. Chem.*, **28** (1988) 76–7.
17. Pfaff, G., Synthesis and characterization of $BaTi_2O_5$. *J. Mater. Sci. Lett.*, **9** (1990) 1145–7.
18. Pfaff, G., Synthesis and characterization of $BaTi_4O_9$. *J. Mater. Sci. Lett.*, **10** (1991) 129–31.