Journal of the European Ceramic Society **12** (1993) 159–164

Wet Chemical Synthesis of $BaSnO_3$ and Ba_2SnO_4 Powders

G. Pfaff

E. Merck, Research & Development, Pigment Division, Frankfurter Strasse 250, D-6100 Darmstadt, Germany

(Received 5 October 1992; revised version received and accepted 11 January 1993)

Abstract

The barium stannates $BaSnO_3$ and Ba_2SnO_4 can be synthesized by the wet chemical peroxide route. The first step of the preparation is the precipitation of stoichiometric peroxo-precursors which are transformable into the corresponding stannates by thermal degradation. The resulting ultrafine, phase-pure barium stannate powders have a small impurity content. They are very sinter active above 1200°C. $BaSnO_3$ shows a better densification behaviour than Ba_2SnO_4 during sintering. A phase $Ba_3Sn_2O_7$ could not be synthesized using the peroxide route.

Die Bariumstannate $BaSnO_3$ und Ba_2SnO_4 können mit der Peroxidmethode auf naßchemischem Weg synthetisiert werden. Der erste Präparationsschritt besteht in der Fällung von stöchiometrischen Peroxo-Precursors, welche durch thermische Zersetzung in die entsprechenden Stannate überführbar sind. Die entstehenden ultrafeinen, phasenreinen Bariumstannatpulver haben nur einen geringen Gehalt an erunreinigungen. Oberhalb von 1200°C sind sie sehr sinteraktiv. $BaSnO_3$ zeigt ein besseres Verdichtungsverhalten als Ba_2SnO_4 beim Sintern. Eine Phase $Ba_3Sn_2O_7$ konnte mit der Peroxidmethode nicht dargestellt werden.

La synthèse par voie humide des stannates de baryum $BaSnO_3$ et Ba_2SnO_4 est possible à partir de peroxydes. La première étape de la préparation est la précipitation des peroxo-précurseurs qui pourront se transformer en stannates correspondants lors du traitement thermique. Les poudres obtenues sont ultrafines, sont constituées de phases pures de stannate de baryum et présentent une tenue en impuretés faible. Elles sont facilement frittables au-dessus de 1200°C. Le comportement à la densification durant le traitement thermique est plus favorable pour $BaSnO_3$ que pour Ba_2SnO_4. La phase $Ba_3Sn_2O_7$ n'a pas pu être synthétisée par cette route peroxyde.

1 Introduction

Alkaline-earth stannates are interesting compounds in particular with regard to their dielectric properties. The solid solutions of $BaTiO_3$–$BaSnO_3$ have received attention in recent years in the field of capacitors.[1,2] Ba(Ti, Sn)O_3 solid solutions are also used for fabrication of ceramic boundary layer capacitors.[3,4] The phase equilibria in the BaO–SnO_2 system have been studied by Wagner and Binder.[5] The existence of the two stable phases $BaSnO_3$ and Ba_2SnO_4 has been reported in their paper. A phase of the composition $Ba_3Sn_2O_7$ was identified in the binary system BaO–SnO_2 at 1400°C by Appendino and Ramonda.[6]

$BaSnO_3$, the most important of these compositions, is a well known dielectric material of technological importance and is normally synthesized at high temperatures of *c.* 1200°C by solid-state reaction between $BaCO_3$ and SnO_2. It crystallizes in the cubic system of perovskite.[7] The high preparation temperatures lead normally to powders of relatively large and varied grain sizes and varying impurity content. There are often problems obtaining phase-pure material because of the intermediate formation of the phase Ba_2SnO_4 during the $BaSnO_3$ synthesis.[5]

Ba_2SnO_4 is found to be stable in the body-centred tetragonal K_2NiF_4 structure, supporting the idea that $BaSnO_3$ accommodates non-stoichiometry in its structure through the formation of alternating layers of perovskite $BaSnO_3$ and rock salt BaO along the c-direction.

$Ba_3Sn_2O_7$ crystallizes in the tetragonal system and is structurally constituted from perovskite double blocks of $BaSnO_3$ alternated with BaO layers.[6] The formation of Ba_2SnO_4 occurs at temperatures of *c.* 1200°C and $Ba_3Sn_2O_7$ is formed at *c.* 1400°C starting from $BaCO_3$ and SnO_2.

There are also few reports on the wet chemical methods of preparing $BaSnO_3$ fine powders.[8,9] So it

Journal of the European Ceramic Society 0955-2219/93/\$6.00

is possible to synthesize $BaSnO_3$ via the precipitated hydrated stannate of the formal composition $BaSnO_3 . 3H_2O$.[8] The evaporation of water during heating occurs up to 300°C, and the first $BaSnO_3$ reflections in the X-ray diffractograms can be seen at temperatures of *c.* 430°C.

Fine $BaSnO_3$ powders consisting of 200–600 nm size crystallites can be prepared at 150–260°C by the hydrothermal method starting from $SnO_2 . H_2O$ gel and $Ba(OH)_2$ solution in Teflon-lined autoclaves.[2,10] $BaSn(OH)_6 . 3H_2O$ is indicated as an intermediate compound during the formation of $BaSnO_3$ under these conditions.

An interesting synthesis to obtain high-purity titanates of calcium, strontium and barium is the peroxide route.[11–17] This wet chemical synthesis occurs via peroxo-precursors like $BaTiO_2(O_2).3H_2O$ for $BaTiO_3$ or $Ba_2TiO_3(O_2).2H_2O$ for Ba_2TiO_4.[11,15] Sintered densities as high as 98% of the theoretical were obtained for some of the so-prepared titanate powders. It is the aim of this paper to investigate the formation of barium stannate powders of various compositions using the peroxide method in analogy to the titanate preparation. The precipitation of the barium and tin containing precursors, their thermal decomposition to the stannates and the characterization of both intermediate products and the final stannate powders as well as the results from sintering experiments are described here.

2 Experimental Procedure

An aqueous solution of $BaCl_2 . 2H_2O$ and $SnCl_4$ (Sn concentration 0·6 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 $BaCl_2 . 2H_2O:SnCl_4:H_2O_2:NH_3$ used were 1:1:2·5:12 for $BaSnO_3$ and 2:1:5:12 for Ba_2SnO_4. Experiments to synthesize the composition $Ba_3Sn_2O_7$ were carried out in a similar manner using the molar ratio 3:2:7:20. 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 temperatures up to 1200°C and in the case of $Ba_3Sn_2O_7$ up to 1400°C.

The dried precursors and the heat-treated powders were investigated by thermogravimetric analysis (TG), differential thermal analysis (DTA), X-ray diffraction (XRD), and chemical analysis (Sn as SnO_2, Ba as $BaSO_4$).

The impurity content of certain elements was measured using atomic absorption spectrometry (AAS) or atomic emission spectrometry (AES). Surface characterization of the titanate powders was carried out by B.E.T. measurements. The fine structure of the powders was obtained by a scanning electron microscope (SEM).

For the sintering experiments, the titanate powders calcined at 1200°C for 1 h 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 80 mesh. The powders were pressed in the form of discs 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.

3 Results

Table 1 contains the results of the analysis of the dried precursors and of the powders obtained after calcination at 1000°C. The peroxo-precursors for

Table 1. Analytical data for the peroxo-precursors and for the products obtained after thermal decomposition at 1000°C (weight loss for 1 h at 1000°C)

Component	*(% exp.)*	*(% calc.)*	*(% exp.)*	*(% calc.)*
	$BaSnO_2(O_2).3H_2O$		$BaSnO_3$	
Barium	36·6	36·7	45·2	45·2
Tin	31·7	31·7	39·1	39·0
Peroxide	8·3	8·6	—	—
Weight loss	18·9	18·7	—	—
	$Ba_2SnO_3(O_2).2H_2O$		Ba_2SnO_4	
Barium	53·9	53·9	60·0	60·1
Tin	23·4	23·3	26·1	26·0
Peroxide	6·1	6·3	—	—
Weight loss	10·5	10·2	—	—
	$Ba_3Sn_2O_5(O_2)_2.5H_2O$		'$Ba_3Sn_2O_7$'	
Barium	46·5	46·6	54·0	54·1
Tin	27·0	26·9	31·3	31·2
Peroxide	7·1	7·2	—	—
Weight loss	14·0	13·8	—	—

$BaSnO_3$ and Ba_2SnO_4 show a stoichiometric composition as well as the stannates. The reactions of the precursor formation can be summarized by the following equations:

$$BaCl_2 + SnCl_4 + H_2O_2 + 6NH_3 + 5H_2O \rightarrow BaSnO_2(O_2).3H_2O + 6NH_4Cl \quad (1)$$

$$2BaCl_2 + SnCl_4 + H_2O_2 + 8NH_3 + 5H_2O \rightarrow Ba_2SnO_3(O_2).2H_2O + 8NH_4Cl \quad (2)$$

The experiment for the formation of a suitable peroxo-precursor for the synthesis of $Ba_3Sn_2O_7$ can be described as follows:

$$3BaCl_2 + 2SnCl_4 + 2H_2O_2 + 14NH_3 + 10H_2O \rightarrow Ba_3Sn_2O_5(O_2)_2.5H_2O + 14NH_4Cl \quad (3)$$

The TG, DTG and DTA curves of the thermal degradation of the two precursors of reactions (1) and (2) are shown in Fig. 1. $Ba_3Sn_2O_5(O_2)_2.5H_2O$ shows a similar behaviour during heating. In all cases there are two stages of weight loss: in a first step up to 280°C the water is evaporated (endothermic effect). The decomposition of the peroxide group of $BaSnO_2(O_2).3H_2O$ occurs between 500 and 700°C and oxygen is released (endothermic effect). The second step of the decomposition of $Ba_2SnO_3(O_2).2H_2O$ is indicated by a weight loss between 550 and 950°C as well as by an endothermic effect.

X-ray diffractograms of the decomposition products of the three precursors as well as of the dried precipitates are shown in Fig. 2. For different calcination temperatures (in each case calcined for 8 h). All precipitates and the powders obtained after heating to 500°C are X-ray amorphous. No reflections can be seen in the diffractograms, because of the very small crystallite sizes. Small reflections appear at 550°C, indicating the formation of stannate phases, SnO_2 or $BaCO_3$. The last two compounds are found in small quantities after decomposition of the peroxo-precursors of reactions (2) and (3) besides Ba_2SnO_4 or $BaSnO_3$ and Ba_2SnO_4. The compounds $BaSnO_3$ and Ba_2SnO_4 are obtained in their pure form upon calcination at 900°C ($BaSnO_3$) and 1000°C (Ba_2SnO_4), respectively. There are no reflections for $Ba_3Sn_2O_7$ in the case of the calcination products of reaction (3) even at temperatures up to 1400°C.

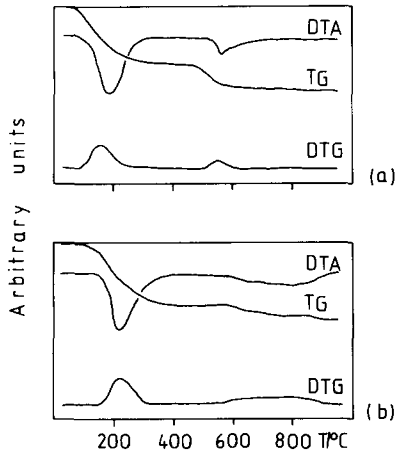

Fig. 1. DTA, TG and DTG curves of (a) $BaSnO_2(O_2).3H_2O$, and (b) $Ba_2SnO_3(O_2).2H_2O$.

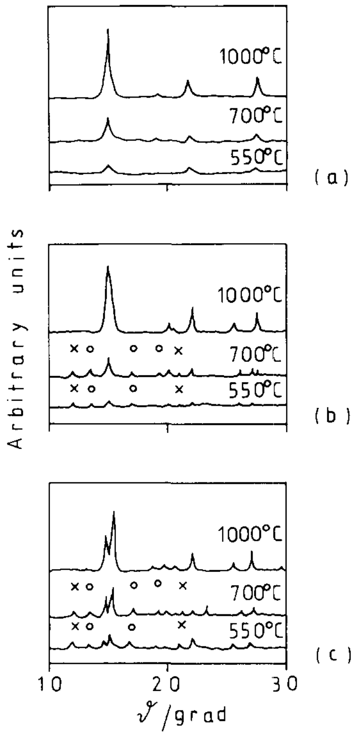

Fig. 2. X-ray diffractograms of the decomposition products of (a) $BaSnO_2(O_2).3H_2O$, (b) $Ba_2SnO_3(O_2).2H_2O$ and (c) $Ba_3Sn_2O_5(O_2)_2.5H_2O$; (×) = $BaCO_3$, (○) = SnO_2.

The specific surface areas and the calculated mean particle sizes for the powders formed during thermal decomposition of the peroxo-precursors for $BaSnO_3$ and Ba_2SnO_4 are shown in Table 2. The values for the titanates obtained after thermal degradation at 1000°C for 1 h are $14\,m^2/g$ for $BaSnO_3$ and $12\,m^2/g$ for Ba_2SnO_4.

The results of sintering experiments are shown in Fig. 3 (1200°C) and Fig. 4 (1400°C). The different green densities ρ_0, of the compacts ($3{\cdot}26\,g/cm^3$ for $BaSnO_3$, $3{\cdot}20\,g/cm^3$ for Ba_2SnO_4) are included by

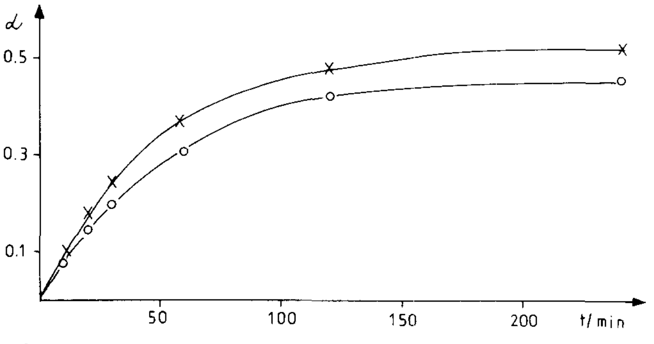

Fig. 3. Densification parameter of (×) $BaSnO_3$ and (○) Ba_2SnO_4 compacts as a function of isothermal heating time at 1200°C.

Table 2. Specific surface area and mean particle diameter dependence on the calcination conditions for the powders obtained during $BaSnO_3$ and Ba_2SnO_4 formation

Conditions (h/°C)	*$BaSnO_3$ formation*		*Ba_2SnO_4 formation*	
	Specific Surface area (m^2/g)	*Mean particle diameter (nm)*	*Specific surface area (m^2/g)*	*Mean particle diameter (nm)*
8/200	98	10	95	10
8/400	72	10	65	10
8/600	42	20	38	20
8/800	25	30	23	40
8/1000	11	80	10	90

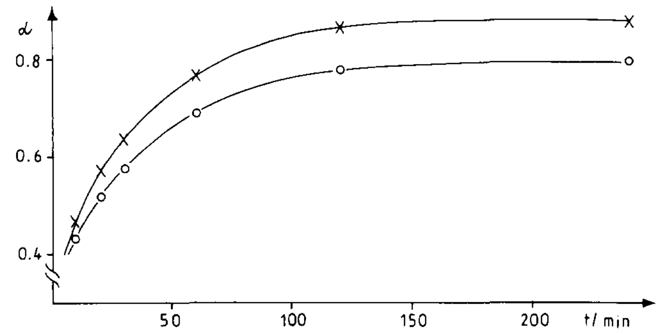

Fig. 4. Densification parameter of (×) $BaSnO_3$ and (○) Ba_2SnO_4 compacts as a function of isothermal heating time at 1400°C.

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°C and 1400°C leads to good densification in all cases increasing in the order $Ba_2SnO_4 < BaSnO_3$. The highest densities after 4 h at 1400°C are 6·74 g/cm^3 for $BaSnO_3$ (93% of ρ_{th}) and 5·94 g/cm^3 for Ba_2SnO_4 (89% of ρ_{th}).

4 Discussion

Barium, strontium and calcium titanates have already been synthesized using the peroxide route.[11-17] It is now possible to obtain new Sn-containing precursors by this method by choosing suitable molar ratios of $BaCl_2 . 2H_2O$, $SnCl_4$, H_2O_2 and NH_3. The composition of these peroxo-precursors are $BaSnO_2(O_2) . 3H_2O$, $Ba_2SnO_3(O_2) . 2H_2O$ and $Ba_3Sn_2O_5(O_2)_2 . 5H_2O$. It is possible to transform $BaSnO_2(O_2) . 3H_2O$ and $Ba_2SnO_3(O_2) . 2H_2O$ into the corresponding stannates by thermal decomposition. The resulting barium stannates $BaSnO_3$ and Ba_2SnO_4 show good stoichiometry and also high purity (main impurities: Al 80 ppm, Ca 80 ppm, Fe 10 ppm, Mg 20 ppm, Mn 20 ppm, Na 110 ppm, Si 30 ppm, Sr 70 ppm).

Thermal degradation of the precursor $Ba_3Sn_2O_5(O_2)_2 . 5H_2O$ at temperatures up to 1400°C leads to mixtures of $BaSnO_3$ and Ba_2SnO_4 in the molar ratio 1:1. The specific surface areas of $BaSnO_3$ and Ba_2SnO_4 obtained after the decomposition of the corresponding precursors at 1000°C for 1 h attain values of about 13 m^2/g. The SEM micrographs of Fig. 5 shows the peroxo-precursor for $BaSnO_3$ and the decomposition products at 550 and 900°C. The powders are strongly agglomerated, and the particle sizes are growing from about 50 nm to 150 nm after the stannate formation. It seems that the particle growth is beginning already at temperatures below 550°C. The stannate powders obtained by the peroxide route show interesting chemical and morphologic properties in comparison with the same compositions synthesized by the solid-state reaction. The impurity content of the powders obtained by the wet chemical route is normally lower, the keeping of stoichiometry is less problematic and the particles are essentially smaller than in the case of the conventionally synthesized stannates.

The thermal degradation of the peroxo-precursors $BaSnO_2(O_2) . 3H_2O$ and $Ba_2SnO_3(O_2) . 2H_2O$ takes place in two steps. The first step in both cases is the evaporation of water. This step is followed by oxygen liberation in the case of the $BaSnO_3$ formation. The decomposition behaviour of $BaSnO_2(O_2) . 3H_2O$ is therefore similar to the situation found for various calcium and strontium containing titanium-peroxo-precursors.[16,17] The second step recorded during the Ba_2SnO_4 formation is the liberation of oxygen and carbon dioxide. The last one is formed by the reaction between the two intermediate products $BaCO_3$ and SnO_2. The X-ray diffractograms show the occurrence of $BaCO_3$ and tin dioxide as intermediate compounds at temperatures between 700 and 900°C only in this case. The detection of $BaCO_3$ at temperatures of about 700 and 900°C during the thermal degradation of $Ba_2SnO_3(O_2) . 2H_2O$ is known likewise for the formation of Ba_2TiO_4 starting from the corresponding peroxo-precursor.[15]

The third precursor $Ba_3Sn_2O_5(O_2)_2 . 5H_2O$ shows another behaviour during thermal decomposition.

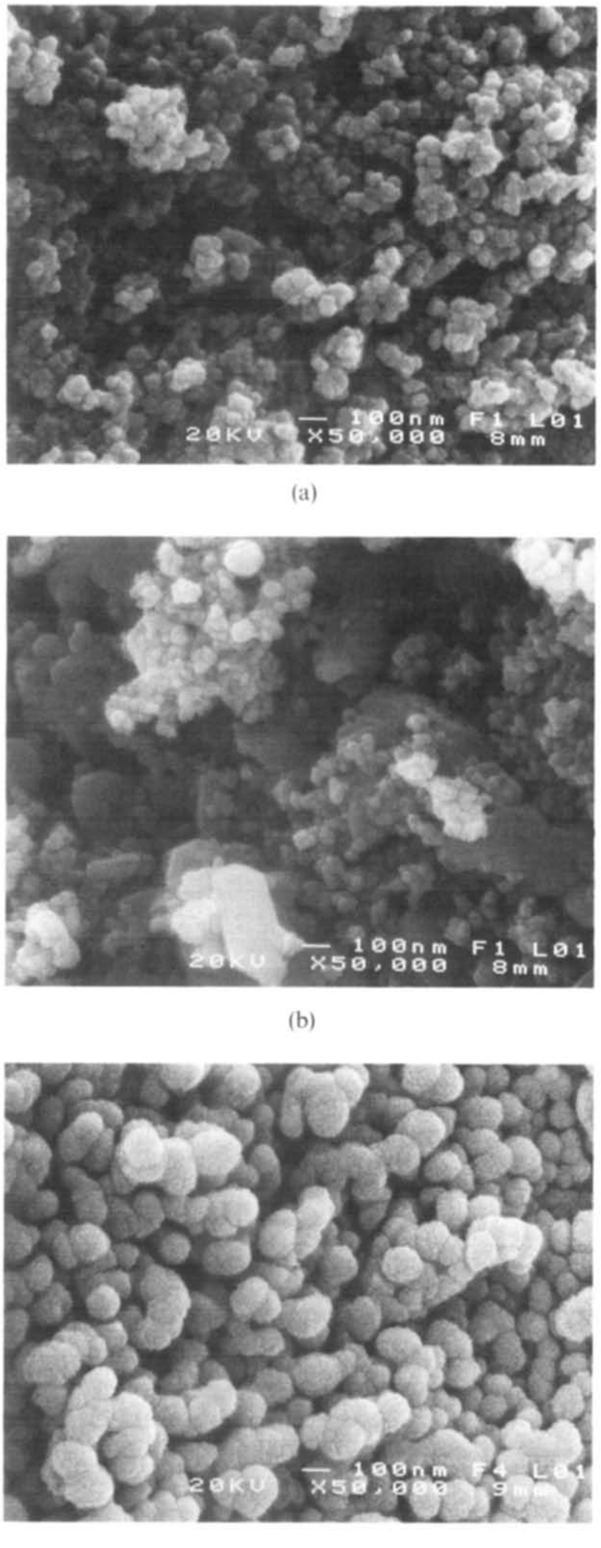

Fig. 5. SEM micrographs of (a) $BaSnO_2(O_2).3H_2O$, (b) powder obtained after calcination of $BaSnO_2(O_2).3H_2O$ at 550°C for 1 h and (c) $BaSnO_3$ obtained after calcination of $BaSnO_2(O_2).3H_2O$ at 900°C for 1 h.

After thermal treatment at 700°C, a diffractogram containing the reflections of $BaSnO_3$, Ba_2SnO_4, $BaCO_3$ and SnO_2 is obtained. At 1000°C, a mixture of $BaSnO_3$ and Ba_2SnO_4 is found in the diffractogram. A quantitative valuation of the reflections shows a $BaSnO_3{:}Ba_2SnO_4$ ratio of 1:1. It is interesting that a mixture of $BaSnO_2(O_2).3H_2O$ and $Ba_2SnO_3(O_2).2H_2O$ shows an analogous behaviour during thermal degradation. There are no indications of the formation of $Ba_3Sn_2O_7$, either as an intermediate or as a final product of the decomposition up to 1400°C.

The sintering behaviour of the barium stannates $BaSnO_3$ and Ba_2SnO_4 formed by the peroxide route is similar to that of the corresponding barium and strontium titanates. $BaSnO_3$, with its cubic perovskite structure, shows the better densification at 1200 and 1400°C. The comparison of the sintering results of the powders described here with those of barium stannates obtained by the solid-state reaction at the same temperatures shows a significantly better sinterability for $BaSnO_3$ and Ba_2SnO_4 formed using the peroxide route. This means that the described peroxide method could be used for the preparation of barium stannates and functional electroceramic elements at distinctly lower temperatures than in the case of the conventional solid-state reaction.

5 Conclusions

$BaSnO_3$ and Ba_2SnO_4 can be synthesized with high purity using the peroxide route. The stannate powders show large specific surface areas and small grain sizes, leading to a high sinterability. $BaSnO_3$ shows a better densification than Ba_2SnO_4 during sintering. Peroxo-precursors of various compositions are formed during the synthesis by a precipitation step from aqueous solutions. All precursors are X-ray amorphous but show definite stoichiometries. The thermal degradation leads directly to the stannate in the case of $BaSnO_3$. $BaSnO_3$, $BaCO_3$ and SnO_2 occur as intermediates during the formation of Ba_2SnO_4 starting from the precursor $Ba_2SnO_3(O_2).2H_2O$. Experiments to obtain the composition $Ba_3Sn_2O_7$ lead to negative results, a stoichiometric precursor is formed likewise, but the thermal decomposition at higher temperatures yields a mixture of $BaSnO_3$ and Ba_2SnO_4 in the ratio 1 : 1.

References

1. Subbarao, E. C., Ceramic dielectrics for capacitors. *Ferroelectrics*, **35** (1981) 143–8.
2. Vivekanandan, R. & Kutty, T. R. N., Hydrothermal synthesis of $Ba(Ti,Sn)O_3$ fine powders and dielectric properties of the corresponding ceramics. *Ceram. Int.*, **14** (1988) 207–16.
3. Wernicke, R., Influence of microstructure on the electrical properties of intergranular capacitors. *Ber. Dtsch. Keram. Ges.*, **55** (1978) 356–8.
4. Brauer, H., Grain-boundary barrier layers in barium metatitanate ceramic with a high effective dielectric constant. (Ger.). *Z. Angew. Phys.*, **29** (1970) 282–7.
5. Wagner, G. & Binder, H., Untersuchung der binären

Systeme BaO–SnO$_2$ und BaO–PbO$_2$. I. Phasenanalysen. *Z. anorg. allg. Chem.*, **297** (1958) 328–46.

6. Appendino, P. & Ramonda, G., Equilibri allo stato solido nel sistema ossido di bario-ossido di stronzio-biossido di stagno. *Ann. Chim. (Rome)*, **61** (1971) 54–60.
7. Wagner, G. & Binder, H., Untersuchung der binären Systeme BaO–SnO$_2$ und BaO–PbO$_2$. II. Kristallstrukturbestimmungen. *Z. anorg. allg. Chem.*, **298** (1959) 12–21.
8. Coffeen, W. W., Ceramic and dielectric properties of the stannates. *J. Am. Ceram. Soc.*, **36** (1953) 207–14.
9. Savos'kina, A. I., Goroshchenko, Y. G. & Selivanova, L. Y., Synthesis of finely divided barium stannate (BaSnO$_3$) from coprecipitation products (Russ.). *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **20** (1984) 472–5.
10. Kutty, T. R. N. & Vivekanandan, R., Barium stannate (BaSnO$_3$) fine powders from hydrothermal preparations. *Mater. Res. Bull.*, **22** (1987) 1457–65.
11. Pfaff, G., Herstellung von BaTiO$_3$-Sinterpulver durch Fällung von BaTiO$_2$(O$_2$).3H$_2$O. *Z. Chem.*, **28** (1988) 76–7.
12. Pfaff, G., Naßchemische Synthese von SrTiO$_3$- und CaTiO$_3$-Sinterpulvern durch Fällung von SrTiO$_2$(O$_2$).3H$_2$O und CaTiO$_2$(O$_2$).3H$_2$O. *Z. Chem.*, **29** (1989) 30–1.
13. Pfaff, G., Synthesis and characterization of BaTi$_2$O$_5$. *J. Mater. Sci. Lett.*, **9** (1990) 1145–7.
14. Pfaff, G., Synthesis and characterization of BaTi$_4$O$_9$. *J. Mater. Sci. Lett.*, **10** (1991) 129–31.
15. Pfaff, G., Synthesis and characterization of Ba$_2$TiO$_4$. *J. Mater. Sci. Lett.*, **10** (1991) 1059–60.
16. Pfaff, G., Peroxide route to synthesize strontium titanate powders of different composition. *J. Eur. Ceram. Soc.*, **9** (1992) 121–5.
17. Pfaff, G., Peroxide route to synthesize calcium titanate powders of different composition. *J. Eur. Ceram. Soc.*, **9** (1992) 293–9.