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Preparation and characterization of titanate powders of different sinterability

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$BaTiO_3$, $SrTiO_3$ and $CaTiO_3$ sintering powders were synthesized using precursors such as $BaTiO(C_2O_4)\cdot 4H_2O$ and $BaTiO_2(O_2)\cdot 3H_2O$, the analogous Sr and Ca compounds, respectively. The titanate powders obtained were characterized with respect to their analytic and granulometric properties. Sintering behaviour was examined in relation to that of $BaTiO_3$, $SrTiO_3$ and $CaTiO_3$ synthesized by the conventional route from carbonates and TiO_2.

1. Introduction

According to the phase diagram, the formation of intermediate stages has to be assumed during the preparation of $BaTiO_3$ from $BaCO_3$ and TiO_2. In the BaO–TiO_2 system, numerous phases exist in the TiO_2-rich flank besides the compounds Ba_2TiO_4 and $BaTiO_3$: $BaTi_2O_5$ [1], $Ba_6Ti_{17}O_{40}$ [2], $Ba_4Ti_{13}O_{30}$ [3], $BaTi_4O_9$ [4], and $Ba_2Ti_9O_{20}$ [5]. Phase relations were further investigated by Rase and Roy [6] and Negas *et al.* [7]. Different phases also appear in the systems SrO–TiO_2 [8, 9] and CaO–TiO_2 [10].

During the reaction of $BaCO_3/TiO_2$ mixtures, for example, a complete loss of CO_2 can be attained at 900 °C. Firstly, a partially inhomogeneous structure exists in which BaO-rich phases, e.g. Ba_2TiO_4, border upon TiO_2-rich phases like $Ba_6Ti_{17}O_{40}$. Because the remaining thermodynamic driving forces are small, and because of kinetically strong inhibited diffusion processes, homogenization requires sintering temperatures up to 1400 °C. Thus in the region with small amounts of excess TiO_2, the melting temperature of the eutectic $BaTiO_3/Ba_6Ti_{17}O_{40}$ at 1320 °C is exceeded, and hence the densification process is favoured. On the other hand, liquid phase sintering promotes inhomogeneous grain growth.

For the formation of a uniform finely grained structure of the ceramics, necessary for example in multilayer capacitors, lower sintering temperatures have to be kept. This can be done by using additives such as Cu_2O/CuO [11, 12]. Another method involves the direct separation of titanates from solutions, or the abridgement of the diffusion paths by the preparation of suitable precursors: titanates are formed from these as very fine powders with high sintering activity, as a result of thermal decomposition at relatively low temperatures.

The use of the titanyloxalates $MeTiO(C_2O_4)_2\cdot 4H_2O$ (Me: Ba, Sr, Ca) as starting materials for the preparation of titanates $MeTiO_3$ has been reported by several authors [13–17]. $BaTiO_2(O_2)\cdot 3H_2O$, and the analogous Sr and Ca compounds, are likewise suitable for this purpose [18–21].

The object of the work presented was to compare the sintering properties of differently prepared $BaTiO_3$, $SrTiO_3$ and $CaTiO_3$ powders which have previously been incompletely described in the literature [22, 23]. The connection between the analytical and granulometric properties of the titanate powders and their sintering behaviour is explained.

2. Experimental procedure

The synthesis of $BaTiO_3$, $SrTiO_3$ and $CaTiO_3$ powders was carried out with chemicals of the highest commercially available purity. The compounds $MeTiO(C_2O_4)_2\cdot 4H_2O$ were formed with a yield of 95% as amorphous white precipitates, when aqueous solutions of $BaCl_2\cdot 2H_2O$, $SrCl_2\cdot 6H_2O$ or $CaCl_2\cdot 6H_2O$ and $TiCl_4$ were given into the threefold volume of an ethanolic solution of oxalic acid at 55 °C (molar ratio $MeCl_2:TiCl_4:H_2C_2O_4 = 1:1:2.4$). Washing with cold water until chloride was not detectable, followed by drying in a dessicator with H_2SO_4 and thermal decomposition for 1 h at 900 °C led to $BaTiO_3$I, $SrTiO_3$I or $CaTiO_3$I.

The light yellow X-ray amorphous compounds $MeTiO_2(O_2)\cdot 3H_2O$ were formed in an argon atmosphere with a yield of 95% by mixing ammonia/H_2O_2 solution with the same volume of aqueous solution prepared from $BaCl_2\cdot 2H_2O$, $SrCl_2\cdot 6H_2O$ or $CaCl_2\cdot 6H_2O$ and $TiCl_4$ (molar ratio $MeCl_2:TiCl_4:H_2O_2:NH_3 = 1:1:2.5:12$) at 10 °C. After washing with water until the chloride was removed, followed by drying, the compounds were decomposed to $BaTiO_3$II, $SrTiO_3$II and $CaTiO_3$II for 1 h at 900 °C.

$BaTiO_3$III, $SrTiO_3$III and $CaTiO_3$III were synthesized from carbonates and rutile in the molar ratio 1:1. The following procedure was used: 5 h dry milling (Fritsch Pulverisette), 2 h calcination at 950 °C, 2 h dry milling, 2 h at 1300 °C.

In order to investigate the sintering process of the different titanate types, the powders were compacted to discs under a pressure of 125 MPa. The discs were sintered under isothermal conditions at 900, 1200 and

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TABLE I Properties of the $BaTiO_3$, $SrTiO_3$ and $CaTiO_3$ powders synthesized by different methods

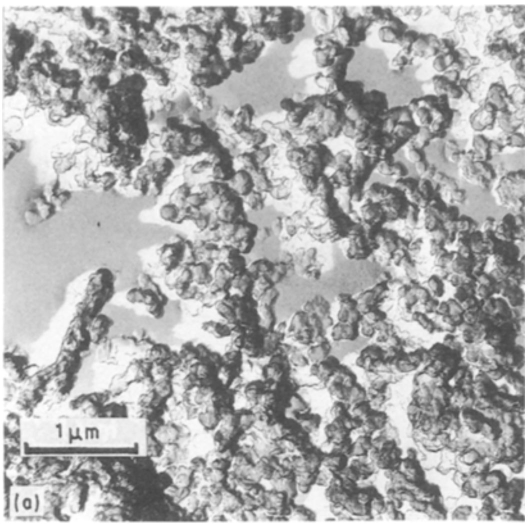
Titanate	Formation conditions ($h\,°C^{-1}$)	S_{BET} ($m^2\,g^{-1}$)	d_{BET} (μm)	d_{ELMI} (μm)	Impurities (p.p.m.)						
					Al	Si	Fe	Pb	V	Mn	Mg
$BaTiO_3$ I	1/900	9	0.11	0.05–0.2	65	20	–	–	–	–	35
$BaTiO_3$ II	1/900	14	0.07	0.05–0.2	100	30	–	5	5	30	50
$BaTiO_3$ III	2/950 + 2/1300	4	0.26	0.2–8	200	60	200	10	5	30	100
$SrTiO_3$ I	1/900	21	0.06	0.05–0.15	80	40	10	–	–	–	20
$SrTiO_3$ II	1/900	15	0.08	0.05–0.15	120	50	10	–	5	20	30
$SrTiO_3$ III	2/950 + 2/1300	4	0.32	0.2–7	240	100	230	10	5	50	90
$CaTiO_3$ I	1/900	12	0.12	0.05–0.15	90	40	10	–	–	–	30
$CaTiO_3$ II	1/900	18	0.08	0.05–0.15	110	50	10	–	5	30	40
$CaTiO_3$ III	2/950 + 2/1300	5	0.29	0.2–7	250	110	220	10	5	60	90

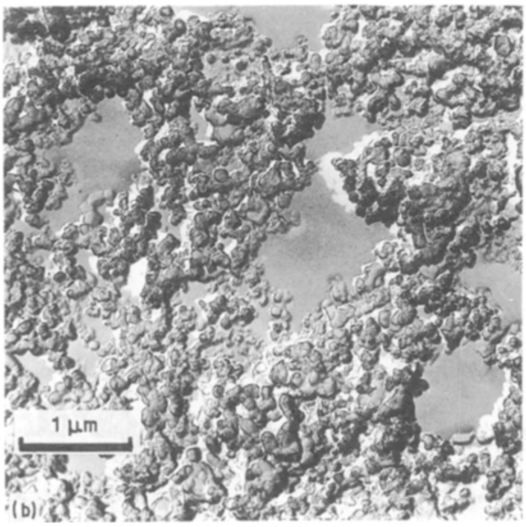
1400 °C in air. The diameter and altitude of three tablets each were measured before and after heating, step by step, utilizing an external micrometer.

Characterization of $BaTiO_3$, $SrTiO_3$ and $CaTiO_3$ powders was carried out by Brunauer–Emmett–Teller (BET) measurement to obtain the specific surface area ("Accusorb 2100 D", Micromeritics, nitrogen adsorption), scanning electron microscopy ("BS 540", Tesla), and atom emission spectroscopy ("PGS 2", Carl Zeiss Jena) to measure the impurity content of certain elements.

3. Results and discussion

Table I shows data on the analytical and granulometric characterization of the prepared titanate types. Powders obtained by thermal decomposition of precursors show, as well as the distinct larger specific surface areas, smaller amounts of impurities than $BaTiO_3$ III, $SrTiO_3$ III and $CaTiO_3$ III. They consist of very small, strongly agglomerated particles with a narrow size distribution. The powders of series III, prepared by the conventional route, are characterized by wide particle size distributions and essentially smaller agglomeration (Fig. 1). Table II shows the sintering data of the titanate types obtained by different methods. After compacting, the samples show green densities ρ_0 which are rising from series I to III. The powders with the smallest grain diameters and narrow size distributions, and with the largest specific surface areas, have an essentially worse densification behaviour than those of series III with coarser particles and wider grain distributions. The various green





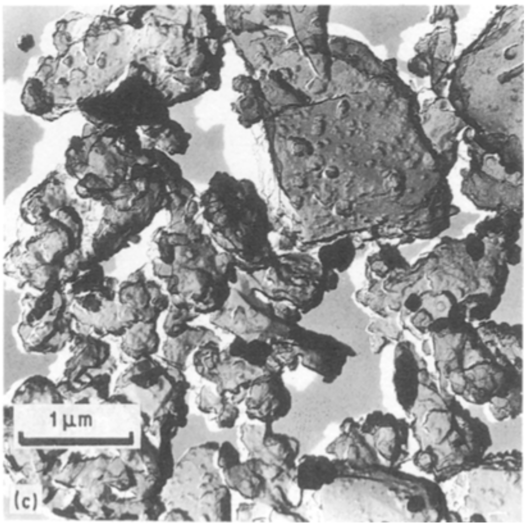


Figure 1 Electron micrographs of $BaTiO_3$ obtained by different methods. (a) $BaTiO_3$ I, (b) $BaTiO_3$ II, (c) $BaTiO_3$ III.

TABLE II Sintering data of the titanate compacts sintered at 900, 1200 and 1400 °C

Titanate	Sintering temperature (°C)	ρ_0 (g cm^{-3})	ρ_{240} (g cm^{-3})	$\alpha_{240} = \dfrac{\rho_{240} - \rho_0}{\rho_{\text{th}}^{a} - \rho_0}$
$BaTiO_3$ I	900	2.55	2.55	0
	1200	2.55	4.13	0.448
	1400	2.55	5.78	0.915
$BaTiO_3$ II	900	2.86	2.86	0
	1200	2.86	4.56	0.528
	1400	2.86	5.93	0.953
$BaTiO_3$ III	900	3.71	3.71	0
	1200	3.71	4.89	0.498
	1400	3.71	5.47	0.743
$SrTiO_3$ I	900	2.37	2.38	0
	1200	2.37	3.32	0.401
	1400	2.37	4.55	0.920
$SrTiO_3$ II	900	2.61	2.62	0
	1200	2.61	3.71	0.516
	1400	2.61	4.60	0.934
$SrTiO_3$ III	900	2.99	2.99	0
	1200	2.99	3.84	0.486
	1400	2.99	4.27	0.731
$CaTiO_3$ I	900	2.24	2.25	0
	1200	2.24	2.99	0.414
	1400	2.24	3.91	0.916
$CaTiO_3$ II	900	2.35	2.36	0
	1200	2.35	3.25	0.531
	1400	2.35	3.97	0.948
$CaTiO_3$ III	900	2.78	2.78	0
	1200	2.78	3.40	0.483
	1400	2.78	3.75	0.765

[a] $\rho_{\text{th}}(BaTiO_3) = 6.08$ g cm^{-3}; $\rho_{\text{th}}(SrTiO_3) = 4.74$ g cm^{-3}; $\rho_{\text{th}}(CaTiO_3) = 4.06$ g cm^{-3}.

densities of the compacts were levelled by using the densification parameter $\alpha = \rho_t - \rho_0/\rho_{\text{th}} - \rho_0$ (where ρ_t is the density in dependence on time and ρ_{th} is the theoretical density) for the calculations and diagrams.

The results of sintering experiments are shown in Figs 2 and 3. At 900 °C, no increase in density was measured for the sintering powders. At 1200 °C (Fig. 2, Table II), a significant densification took place in all cases. The strongest increase in density occurred for specimens of series II, which were obtained from peroxide precursors.

Isothermal sintering at 1400 °C effects an essentially faster densification, and high final densities for titanates synthesized by wet chemical methods with their smaller grain diameters and larger specific surface areas.

Light micrographs demonstrate, moreover, that no further grain growth appears in the case of titanate

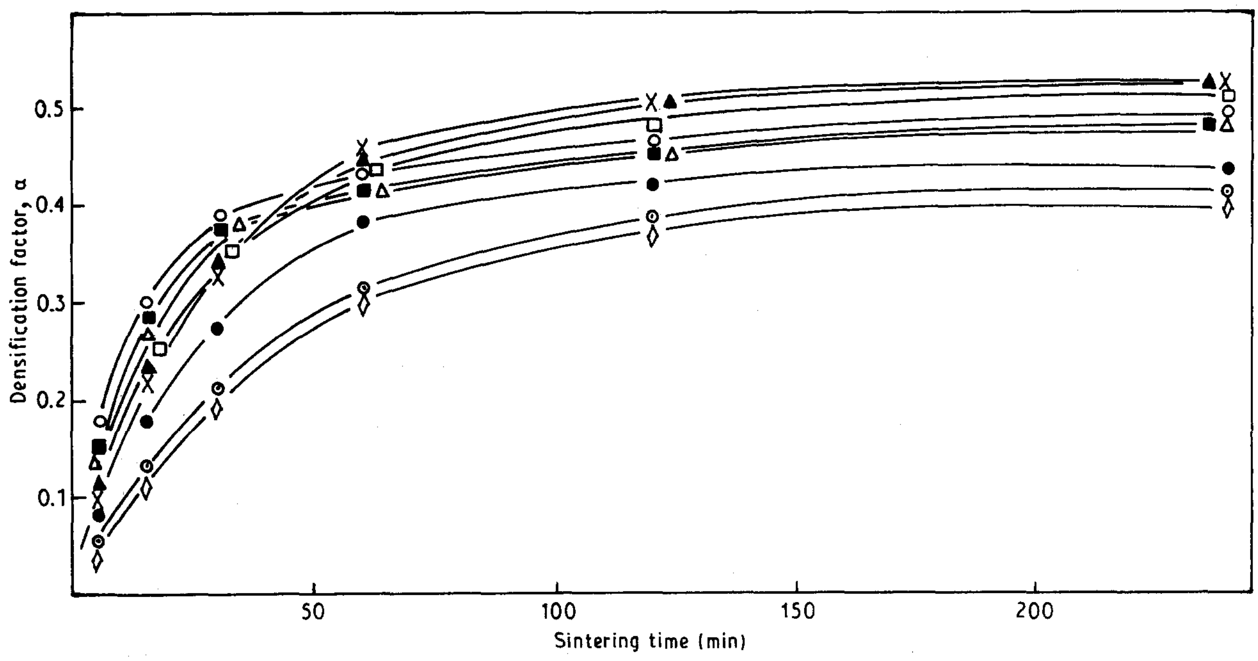


Figure 2 Densification parameter α of $BaTiO_3$, $SrTiO_3$ and $CaTiO_3$ samples as a function of isothermal heating time at 1200 °C: ●, $BaTiO_3$ I; ×, $BaTiO_3$ II; ○, $BaTiO_3$ III; ◇, $SrTiO_3$ I; □, $SrTiO_3$ II; △, $SrTiO_3$ III; ⊙, $CaTiO_3$ I; ▲, $CaTiO_3$ II; ■ $CaTiO_3$ III.

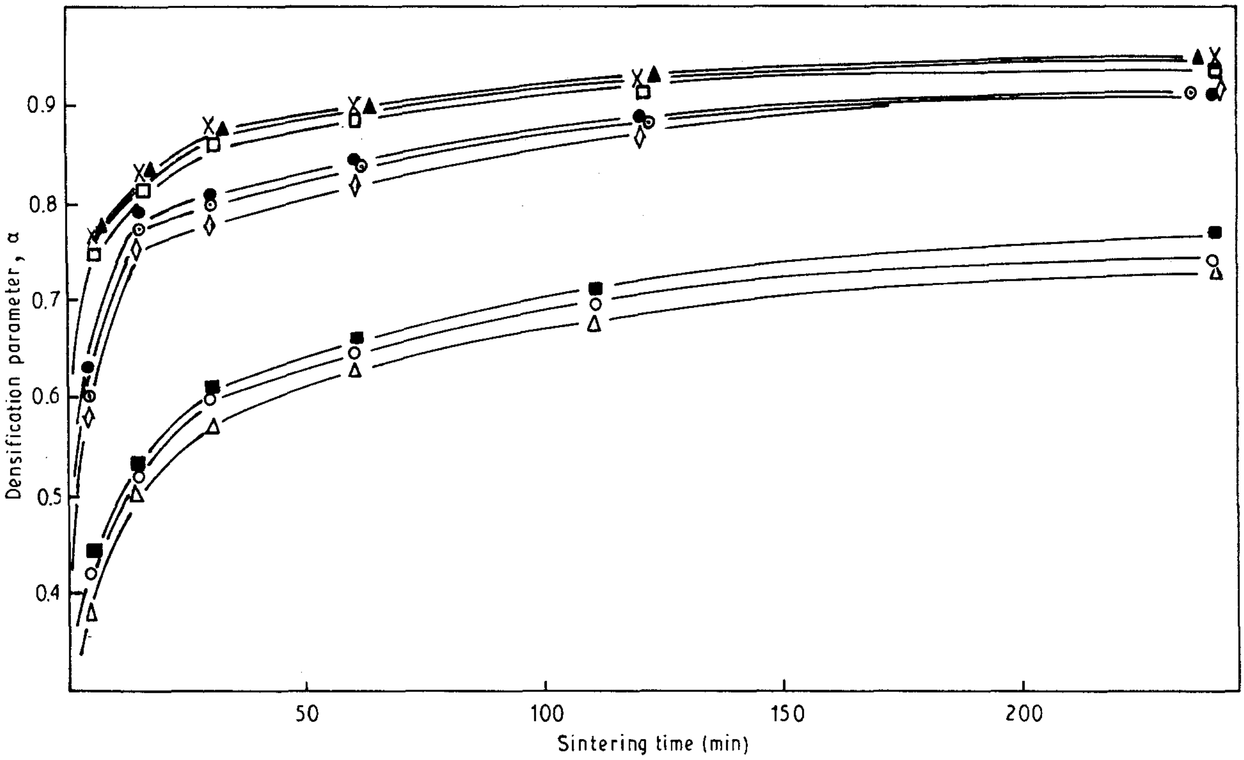


Figure 3 Densification parameters of $BaTiO_3$, $SrTiO_3$ and $CaTiO_3$ samples as a function of isothermal heating time at 1400 °C (for symbols see Fig. 2).

samples sintered up to 8 h at 1200 °C. The grain diameters reach values between 1 and 10 μm only for $BaTiO_3$ III, and between 1 and 5 μm for $SrTiO_3$ III and $CaTiO_3$ III. On the contrary, a strong increase in grain diameter and an extreme decrease in the number of grain boundaries occurs at 1400 °C in all cases. The grain diameters grow up to 20 μm in the case of $BaTiO_3$ III. Inhomogeneous grain growth is observed for all specimens. The favourable granulometric situation is one reason for the better sintering of $MeTiO_3$ I and $MeTiO_3$ II powders. Because of the very small and uniform particles, relatively small pores occur in the green disc-shaped specimens after compacting. In particular, above 1200 °C this leads to fast sintering with strong shrinkage already in the first sintering phase, where the contacts are formed. Grain boundary diffusion can be assumed as the most probable mechanism for this initial stage. The relatively favourable densification behaviour of $BaTiO_3$ III, $SrTiO_3$ III and $CaTiO_3$ III up to 1200 °C can be attributed to the comparatively high green densities which involve narrow contacts or large contact areas between the particles. A greater part in volume diffusion has to be taken into consideration at 1200 °C for the titanate powders of series III with their larger grains.

At 1400 °C, an extremely fast densification occurs, together with the disappearance of small pores and an enormous grain growth for the samples $MeTiO_3$ I and $MeTiO_3$ II. A change in the sintering mechanism from grain boundary diffusion to volume diffusion after a short time is likely. Hoeffgen *et al.* [24] have found, using geometrical statements, that for relatively fine barium titanate powders at lower temperatures, grain boundary diffusion (and at higher temperatures volume diffusion) dominates by isothermal sintering. On the other hand, they calculated that volume diffusion already predominates at lower sintering temperatures in coarser $BaTiO_3$ powders. Their experiments were carried out with $BaTiO_3$ prepared from barium titanyl oxalate. The mathematical interpretation of our results does not show such a good correspondence with the theoretical statements of Kingery [25] or Johnson [26], where according to the equations

$$\Delta L/L_0 = Kt^{1/n}$$

and

$$\log(\Delta L/L_0) = K' + 1/n \log t$$

(where K and K' are constants, $\Delta L/L_0$ is the relative longitudinal deformation, and t is the time), the mechanism of sintering can be discussed using the value of n ($n = 3$ for grain-boundary diffusion; $n = 2$ for volume diffusion) [26–28]. The n values from our sintering experiments were always less than 2. The likely explanation is on the one hand, the granulometric situation, which does not correspond to a model system consisting of spherical particles; and on the other hand, the influence of other mechanisms, e.g. liquid phase sintering.

Impurities in the $BaTiO_3$, $SrTiO_3$ and $CaTiO_3$ powders are accumulated during the sintering process, in particular at the grain boundaries. There they contribute to grain-boundary diffusion. On the other hand, the well-known formation of liquid phases occurs due to the impurities. Regarding the Ba- and/or Ti-containing compositions, eutectics exist at the compositions

$(BaO)_{0.25}(TiO_2)_{0.25}(SiO_2)_{0.5}$	at 1250 °C	[29]
$(BaO)_{0.2}(Al_2O_3)_{0.2}(SiO_2)_{0.6}$	at 1311 °C	[30]
$(MnO)_{0.5}(SiO_2)_{0.11}(TiO_2)_{0.39}$	at 1120 °C	[31]

Similar phases are provable in the Sr- or Ca-containing systems [32–35]. The conventionally prepared titanates of series III possess by far the largest amounts of impurities. The quantity of liquid phases is consequently higher than in the case of the purer $MeTiO_3$ powders. Hence the densification promoting effect combats the disadvantages of these powders resulting from the granulometric situation, so that relatively high final densities are also reached for these powders.

Consequently, the sintering process of the $BaTiO_3$ powders represents a very complex phenomenon, in which, as well as morphologic properties, certain impurities play an important role.

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