

Preparation, characterization and sintering behavior of barium titanate powders coated with Ba-, Ca-, Si- and Ti-containing components

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Abstract

An emulsion technique and spray drying were used to prepare BaTiO₃ powders coated with additives. Different additive compositions (TiO₂; TiO₂/SiO₂; CaO/TiO₂/SiO₂; 2BaO/TiO₂/2SiO₂) were used in the form of their aqueous precursor solutions. The as-received powders were compared with powders of the same composition manufactured by conventional wet-milling. The coating of the BaTiO₃ powder positively influences the sintering behavior. Isothermal dilatometric measurements show that the activation energy ΔE of the shrinkage of the coated powders is lower than that of the powders prepared by milling. This is caused by the homogeneous distribution of the additive. The activation energy for the different additives changes in the following sequence: $\Delta E(2\text{BaO}/\text{TiO}_2/2\text{SiO}_2) < \Delta E(\text{TiO}_2) < \Delta E(\text{CaO}/\text{TiO}_2/\text{SiO}_2) < \Delta E(\text{TiO}_2/\text{SiO}_2)$. This sequence correlates with the amount of Ba ions necessary to diffuse out of the BaTiO₃ matrix to form the secondary phases Ba₂TiSi₂O₈ or Ba₆Ti₁₇O₄₀, respectively. © 1997 Elsevier Science S.A.

Keywords: Barium titanate; Coating; Spray drying; Preparation; Sintering; Dilatometry

1. Introduction

In the production of functional and structural ceramics additives are used to control the microstructure and the properties of the grain boundaries of the final ceramic. The distribution of these sintering aids and/or grain boundary modifiers in the starting powder is usually realized by milling. But in the best case a random homogeneous mix results. The homogeneity scale depends on many factors, e.g. density, particle size, particle shape of the starting powder and the additive.

An alternative to milling is 'ordered mixing', i.e. the preparation of core-shell-like structures of the matrix powder with the additive. These two types of mixtures are illustrated in Fig. 1 schematically.

In recent years many papers [1–12] dealt with the coating of ceramic starting powders. The coating of the starting powders was investigated for AlN [1], Si₃N₄ [2–4], ZrO₂ [5,6], SnO₂ [7] and Al₂O₃ [8–10] systems. The preparation of these coatings was performed in most cases by solution chemistry methods, either by precipitation from aqueous solution changing the pH [1,4–6,11], or by hydrolysis of alkoxide

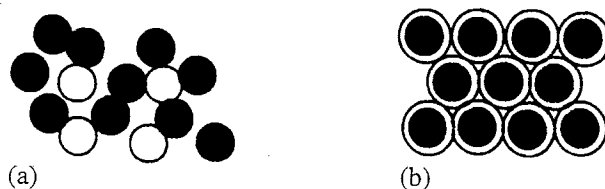


Fig. 1. Schematic distribution of the additive (white) in the starting powder (black) after milling (a) and coating (b).

solution [3,7,10–12] of the suspension. The electrophoretic coating was also described [2,8].

The coating of BaTiO₃ powders was investigated by Selmi and Amarakoon [7], Ogata [11] and Abicht et al. [12]. Selmi and Amarakoon [7] describe the coating of BaTiO₃ powders with a sol-gel composition containing dopants (Y), counterdopants (Mn, F) and sintering aids (Si). The properties of the final ceramics are reported, but without any comparison with ceramics conventionally prepared. The influence of the coating during the sintering is not discussed. Ogata [11] claims the process of coating of the powders only, without considering the manufacture of the ceramics. Abicht et al. [12] report that a smaller amount of SiO₂ (compared with the conventional ceramic mixed oxide method) is necessary to get similar properties of the final ceramics if silica is added by the hydrolysis of tetraethylorthosilicate.

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Table 1
Starting materials for the additives used in the different preparation methods

Additive composition	Milling	Spray drying, emulsion technique
2BaO/TiO ₂ /2SiO ₂	BaCO ₃ + TiO ₂ + SiO ₂	Ba(NO ₃) ₂ + TiCl ₄ + silica sol
CaO/TiO ₂ /SiO ₂	CaCO ₃ + TiO ₂ + SiO ₂	Ca(NO ₃) ₂ + TiCl ₄ + silica sol
TiO ₂ /SiO ₂	TiO ₂ + SiO ₂ or TiO ₂ /SiO ₂ hydrogel	TiCl ₄ + silica sol
TiO ₂	TiO ₂	TiCl ₄

It is known that titania and silica additives influence the microstructure of semiconducting BaTiO₃ ceramics. These additives react with the BaTiO₃ powder during sintering. Thus, titania reacts with BaTiO₃ to give Ba₆Ti₁₇O₄₀. The new system BaTiO₃/Ba₆Ti₁₇O₄₀ forms a eutectic melt at 1320°C [13]. In silica-containing BaTiO₃-based ceramics a liquid phase forms already at about 1245°C [14–16]. This liquid phase has the composition 24 mol% SiO₂, 46 mol% BaO, 30 mol% TiO₂ [16], with Ba₂TiSi₂O₈ (fresnoite) being one ingredient of the eutectic mixture.

The addition of calcia modifies the microstructure of BaTiO₃ ceramics by occupying A-sites in the perovskite ABO₃, thus forming solid solutions (Ba,Ca)TiO₃ [17,18]. Under certain circumstances a B-site substitution is also possible leading to drastic changes of the electric properties [19].

In the present work here we used single- and multi-component additives to coat BaTiO₃ powder. TiO₂, TiO₂/SiO₂, 2BaO/TiO₂/2SiO₂ (BTS) and CaO/TiO₂/SiO₂ (CTS) precursors were chosen.

The problem of chemical precipitation methods for coating of powders is to make sure that the surface of the powder itself is covered and no separate precipitation of the pure additive occurs.

We used two coating methods to realize this by creating, minimizing and isolating of individual microreactors. This was done in the emulsion technique (method 1) by controlling the droplet size of the aqueous component in the organic phase, and in the spray-drying method (method 2) by the spray velocity. For the purpose of comparison the conventional milling/mixing of the starting BaTiO₃ powder and the additives (method 3) has also been used.

2. Experimental

The BaTiO₃ starting powder used in this study was prepared by conventional mixed oxide technique. Mixtures of BaCO₃ (Leuchtstoffe und Feinchemikalien GmbH, Bad Liebenstein) and TiO₂ (Merck 808) were calcined for 2 h at 1100°C, followed by milling. For the synthesis of the aqueous solutions of the coating components the following reagent grade chemicals were used: TiCl₄ (Merck-Schuchardt 812382), silica sol (Levasil 200S/30%, Bayer-Werke Leverkusen), Ca(NO₃)₂ and Ba(NO₃)₂ (Laborchemie Apolda). The coating solutions were obtained by hydrolysis of TiCl₄ at about 4°C and adding of the Si, Ba and/or Ca components to the sol yielding the precursor composition TiO₂, TiO₂/

SiO₂, CaO/TiO₂/SiO₂ or 2BaO/TiO₂/2SiO₂, respectively. Table 1 summarizes the raw materials of the additives for the different preparation methods. The aqueous coating suspensions were prepared to give 1 g BaTiO₃/10 ml coating solution. The concentrations of the coating solutions were adjusted so that the molar ratios of the coating components and the BaTiO₃ powder were 4:96 for the TiO₂/BaTiO₃, TiO₂-SiO₂/BaTiO₃ and CaO-TiO₂-SiO₂/BaTiO₃ systems, and 2:98 for the 2BaO-TiO₂-2SiO₂/BaTiO₃ system, respectively.

2.1. Emulsion technique (method 1)

A combination of suspension and emulsion was used for the coating of the BaTiO₃ powders. We modified the microemulsion system described by Burgard [20]. The modified system consists of petroleum ether (50–70°C)–emulsifier BRIJ-30 (ICI Specialty Chemicals)–octanol in the composition of 80:11:9 (in vol.%). The aqueous phase (20 vol.% of petroleum ether) was loaded with the suspended BaTiO₃ powder and the dissolved coating components.

The emulsion was prepared by stirring (5 min) the mixture of the liquids and then emulsifying (5 min) with an ultrasonic disintegrator (Fa. Branson). After that the gel formation in the aqueous phase was initiated by flowing in of gaseous NH₃. A short aging time of 5–10 min followed and after the addition of 10 vol.% n-butanol (relative to the aqueous phase) the water was eliminated by azeotropic distillation. The residue was tempered at 350°C for 5 h.

2.2. Spray drying (method 2)

A mini spray dryer 190 (Fa. Büchi) was used. The instrumental conditions (heating, aspirator) were adjusted so that a constant input temperature of 210°C and an output temperature of 115°C of the air were achieved. The flow velocity of the suspension was 2.5 ml min⁻¹. The spray-dried powders were tempered at 350°C for 5 h to ensure comparability with the powders obtained by method 1.

2.3. Milling method (method 3)

The BaTiO₃ starting powder was mixed with the different additives in a ball mill for 24 h. The raw materials for the additives were BaCO₃, TiO₂, SiO₂ (Suprasil, precipitated silica) and CaCO₃ (Leuchtstoffe und Feinchemikalien GmbH, Bad Liebenstein). In one case we used a TiO₂/SiO₂/

hydrogel. This hydrogel was prepared from TiCl_4 sol and silica sol, gelled by addition of aqueous NH_3 solution and washed until free of Cl^- ions.

2.4. Characterization

The coated powders were investigated using a scanning electron microscope (JEOL 6400F, equipped for energy dispersive X-ray spectrometry (EDX)). The particle size distribution (Shimadzu, SA-CP-3) of the powders was determined using a 0.2 wt% $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ peptisator solution. The specific surface area (BET) was measured using an ASAP-2400 (micromeritics). The sintering behavior was studied in situ by dilatometry. The powders were isostatically pressed into disks of 60% of theoretical density. The dilatometric investigations were performed with a dilatometer L75/44 (Linseis) in air with a heating rate of 10 K min^{-1} . The isothermal dilatometric measurements (1050°C , 1100°C , 1150°C , 1200°C) were carried out with a TMA 92 (Setaram) apparatus (load 1 g).

3. Results and discussion

The starting BaTiO_3 powder was characterized by XRD and SEM. It represents the highly crystalline, tetragonal mod-



Fig. 2. Scanning electron micrograph of BaTiO_3 powder obtained by conventional mixed oxide method ($\text{BaCO}_3 + \text{TiO}_2$, calcination 1100°C , 2 h).



Fig. 3. Scanning electron micrograph of BaTiO_3 powder coated with $\text{TiO}_2/\text{SiO}_2$ prepared by emulsion technique.

ification of barium titanate, which consists of primary particles of 500 nm size (SEM, Fig. 2, BET). The primary particles are agglomerated to a average grain size of about $1.7 \mu\text{m}$. The surface of the primary particles is smooth and the edges are well detectable and sharp.

The electron micrographs of the starting powder with $\text{TiO}_2/\text{SiO}_2$ additives prepared by emulsion technique, spray drying and milling method are shown in Figs. 3–5. The powders prepared by methods 1 and 2 show a complete wrapping of the grains by the additive. The initial surface characteristic



Fig. 4. Scanning electron micrograph of BaTiO_3 powder coated with $\text{TiO}_2/\text{SiO}_2$ prepared by spray drying method, (a) original magnification $5000\times$ (b) original magnification $15000\times$. (Reduced in reproduction by 74%.)



Fig. 5. Scanning electron micrograph of BaTiO_3 powder mixed with $\text{TiO}_2/\text{SiO}_2$ hydrogel by milling.

of the BaTiO_3 powder has changed. The surface is slightly roughened and the edges are rounded (Figs. 3 and 4(b)). On the other hand, the microstructure of the mixture of BaTiO_3 and $\text{TiO}_2/\text{SiO}_2$ gel obtained by milling is illustrated in Fig. 5. It shows the inhomogeneity of the mill-mixed powder, that is characterized by the coexistence of the original BaTiO_3 grains with smooth surfaces and small and large gel particles. In the gel particles with a structured surface Ti and Si were detected as main components by EDX. The small gel particles are loosely deposited on the surface of the BaTiO_3 grains.

The BET measurements confirm the covering of the surface of the starting BaTiO_3 powder by the additive prepared by emulsion technique. This is exemplarily explained for the CTS-coated powder. The BET surface of the starting BaTiO_3 powder was determined to be $2.63 \text{ m}^2 \text{ g}^{-1}$; that of the pure CTS powder prepared by emulsion technique is $170.8 \text{ m}^2 \text{ g}^{-1}$. Taking into account the mass ratio of the two constituents in the product prepared one can calculate the specific surface of the resulting product with respect to two extreme situations. First, the two constituents coexist side by side, and secondly, the CTS additive completely covers the surface of the BaTiO_3 starting powder. The value for the first case is calculated to be $10.62 \text{ m}^2 \text{ g}^{-1}$, whereas that of the second case is $8.12 \text{ m}^2 \text{ g}^{-1}$. The experimentally determined value is $8.23 \text{ m}^2 \text{ g}^{-1}$, indicating the covering of the BaTiO_3 starting powder. The BET specific surfaces of the powders prepared by method 3 are greater than the values calculated for the first extreme. We explain this with the milling effect during the preparation. This milling effect was also proved by the grain size analysis. The average grain size of the powders prepared by method 3 was $1.1 \mu\text{m}$ compared to $1.7 \mu\text{m}$ in the starting powder.

The average grain size of the spray-dried powders is about $4 \mu\text{m}$. These particles represent agglomerates, and the droplet

size and shape of the sprayed suspension are preserved in the dried product. This is clearly seen in the electron micrograph (Fig. 4(a)). The particles consist of hollow spheres of coated BaTiO_3 grains adhered by the coating.

The main investigations were focused on the sintering behavior of the modified BaTiO_3 powders in order to clarify the influence of the different preparation method and the effect of the various additives.

In Fig. 6 the shrinkage curves of mixtures 96 mol% BaTiO_3 + 4 mol% $\text{TiO}_2/\text{SiO}_2$ prepared by methods 1, 2 and 3 are presented. The coefficient of expansion is plotted versus the temperature. Because heating was performed with a constant rate the coefficient of expansion may be correlated with the shrinkage rate.

Three facts are noteworthy:

1. The shrinkage rate $v_s = \Delta(\Delta L/L_0)/\Delta t$ at the maximum is very high ($v_s = 2.5\text{--}5.0 \times 10^{-4} \text{ s}^{-1}$). Such high shrinkage rates cannot be explained by diffusion processes [21]. If the diffusion determines the shrinkage process only (diffusion viscous flow) shrinkage rates are supposed to be $10^{-8}\text{--}10^{-5} \text{ s}^{-1}$ [22].
2. The shrinkage is complete before the sintering temperature reaches the eutectic temperature of 1245°C (in SiO_2 -containing BaTiO_3 ceramics [14–16]). The shrinkage process proceeds without any liquid phase. The density of the compacts below 1245°C is 90–95% of the theoretical density.
3. There are distinctive differences in the shrinkage behavior between the powders prepared by methods 1 and 2, and the powder prepared by method 3 on the other hand. The shrinkage of the powders prepared by spray drying and emulsion technique starts already at 950°C and has a maximum in the shrinkage rate at 1120°C . The ‘milled’ powder

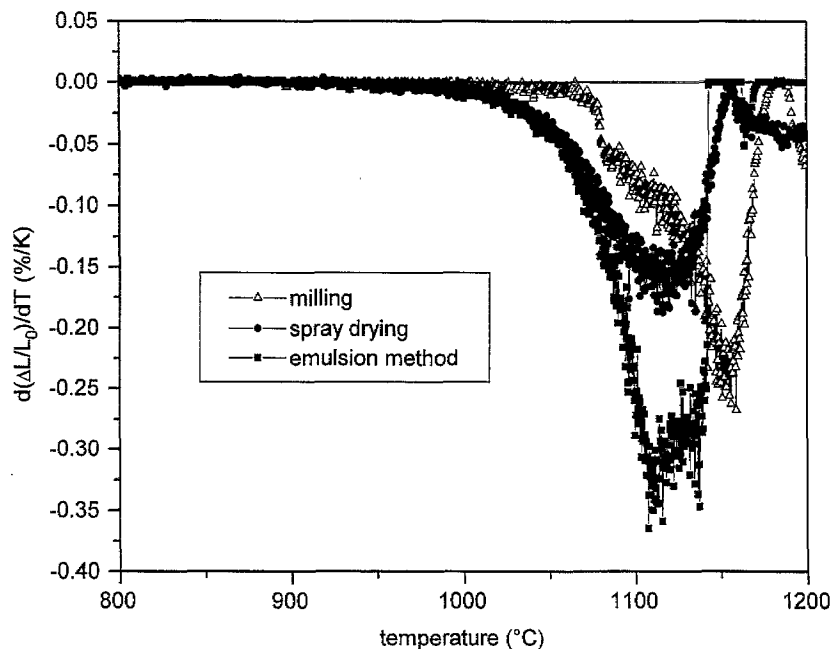


Fig. 6. Coefficient of expansion of green compacts of BaTiO_3 powders with $\text{TiO}_2/\text{SiO}_2$ additives prepared by different methods as a function of temperature.

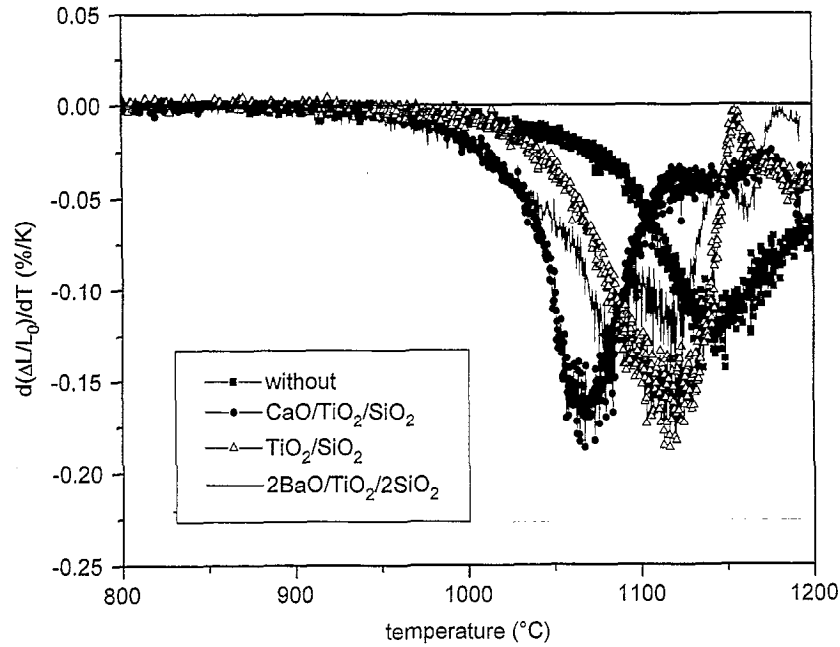


Fig. 7. Coefficient of expansion of green compacts of spray dried BaTiO_3 powders with different additives as a function of temperature.

compacts begin to shrink at 1050°C and the maximum is at 1150°C (with a shoulder at 1100°C).

Fig. 7 shows the shrinkage behavior of green compacts of spray dried BaTiO_3 powders with different additives. It is clearly seen that the maximum of the shrinkage rate shifts to lower temperatures when the BaTiO_3 powder is coated with SiO_2 -containing additives. The temperatures of the maxima of the shrinkage rate are in the $\text{CaO/TiO}_2/\text{SiO}_2$, $2\text{BaO/TiO}_2/2\text{SiO}_2$ and $\text{TiO}_2/\text{SiO}_2$ additive system at 1067°C , $1080^\circ\text{C}/1110^\circ\text{C}$ and 1120°C , respectively. It is noteworthy that in the case of the coating with the $2\text{BaO/TiO}_2/2\text{SiO}_2$ precursor the shrinkage at low temperatures is more pronounced than for the other additives.

Isothermal dilatometric measurements were performed to verify the shrinkage mechanism and to quantify the activation energy for the shrinkage process. The simple model of Kingery [23] was used to evaluate the experimental data.

Plotting the logarithm of relative change in length, $\Delta L/L_0$, versus the logarithm of time t for the different temperatures according to Eq. (1), one will get a system of curves whose slope $1/n$ is related to the sintering mechanism.

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

$K = \text{constant}$, $n=1$ for viscous flow, $n=2$ for volume diffusion, $n=3$ for grain boundary diffusion.

The activation energy ΔE of densification is given by Eq. (2).

$$K = K_0 \exp(-\Delta E/kT) \quad (2)$$

One of these isothermal shrinkage curves is presented in Fig. 8. It is seen that the shrinkage process is divided into two sections representing different shrinkage mechanisms. This division into two sections is characteristic for all preparation methods, all used additives and all investigated temperatures.

The slope of the graph in the first shrinkage section ($t=0-10$ min) is 1. This section is characterized by viscous flow, and represents the main part of the whole shrinkage. In the second section ($t=20-100$ min) the volume and/or grain boundary diffusion is dominant ($n=2-3$). That means the whole shrinkage process is determined by sliding and diffusion processes.

We calculated the activation energies ΔE for the first section of isothermal shrinkage. They are summarized in Table 2 for the powders prepared by methods 2 and 3 with different additives. Two tendencies are visible. Firstly, the activation energies of the spray-dried powders are lower than those of the 'milled' powders. Secondly, if we compare the activation energies of the different additives we get the following sequence in both preparation methods:

$$\Delta E(\text{BTS}) < \Delta E(\text{TiO}_2) < \Delta E(\text{CTS}) < \Delta E(\text{TiO}_2/\text{SiO}_2)$$

How can one explain these experimental results?

The additives were dispersed homogeneously over the whole surface of the BaTiO_3 starting powder by spray drying and emulsion method producing an amorphous shell. These BaTiO_3 core-additive shell structures positively influence the main shrinkage stage of sintering. From the isothermal dilatometric measurements and from the high value of the shrinkage rate [22] it may be concluded that this sintering stage is characterized by sliding of whole powder particles into the pores. Such sliding processes were postulated and investigated by Geguzin [24] and Schatt [25].

The slidability requires a certain flexibility of the grain boundary layer, which is given by the complete covering of the surface and the amorphous status of the additive.

In the 'milled' (method 3) powders the additives are randomly distributed in the mixture so that local similar conditions are existent as described above but on the other hand

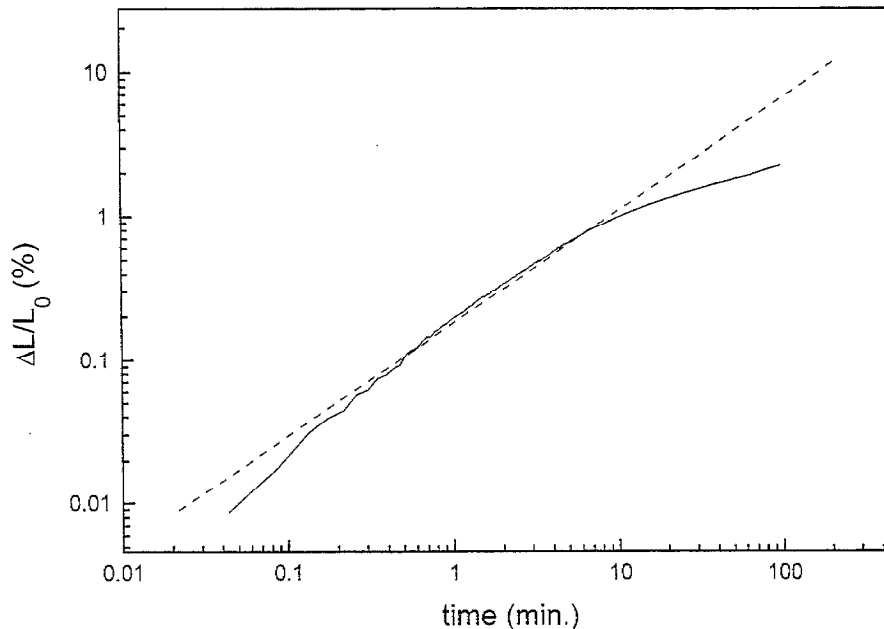


Fig. 8. Isothermal shrinkage curve of spray dried mixture 96 mol% BaTiO₃ + 4 mol% CaO/TiO₂/SiO₂ at 1200°C.

Table 2

Activation energies of the densification process of BaTiO₃ powders with different additives (in kJ mol⁻¹)

Preparation method	2BaO/TiO ₂ /2SiO ₂	TiO ₂	TiO ₂ /SiO ₂	CaO/TiO ₂ /SiO ₂
Spray drying	310.8	345.4	575.3	429.0
Milling	258.2	550.6	1262.6	673.8

most BaTiO₃ particles abut upon each other. The direct BaTiO₃-BaTiO₃ contact hinders the sliding process. This is evident in the existence of two maxima in the shrinkage rate (Fig. 6) and consequently in the higher activation energy for the shrinkage.

The sequence of the activation energies for the different additives one can explain as follows. In all SiO₂-containing BaTiO₃ ceramics crystalline fresnoite (Ba₂TiSi₂O₈) was found [12,26] as secondary phase. The lowest activation energy was determined for the 2BaO/TiO₂/2SiO₂ additive. With the addition of this precursor the material composition for the formation of fresnoite is given instantaneously. Fresnoite was detected in the BTS-containing powders by X-ray diffraction starting at 950°C.

In the case of TiO₂/SiO₂ and CaO/TiO₂/SiO₂, and in the case of the TiO₂ additives, the diffusion of Ba²⁺ ions out of the BaTiO₃ matrix is necessary to yield Ba₂TiSi₂O₈ and the Ba₆Ti₁₇O₄₀ phase, respectively. The amount of Ba²⁺ ions (per unit TiO₂ of the additive) required for the formation of corresponding secondary phases increases from TiO₂ to CaO/TiO₂/SiO₂ and TiO₂/SiO₂. That means the amount of diffusing Ba²⁺ ions influences the shrinkage behavior and correlates with the activation energy.

4. Conclusions

Two techniques were investigated for coating of BaTiO₃ powders, a modified emulsion technique and spray drying.

The coating additives were applied in the form of their aqueous precursor solutions whose compositions correspond to TiO₂, TiO₂/SiO₂, CaO/TiO₂/SiO₂ and 2BaO/TiO₂/2SiO₂. Powders of the same composition were prepared by conventional milling of the starting BaTiO₃ powder and the additive to draw a parallel. The emulsion technique and the spray-drying method were found to result in covering of the surface of the BaTiO₃ powder by the additive, whereas milling leads to a side-by-side distribution of BaTiO₃ powder and additive, only. The coating of the BaTiO₃ powders influences the densification behavior of the compacts positively. The densification is determined by sliding and diffusion processes. Isothermal dilatometric measurements show that the activation energy ΔE of the densification of the coated powders is lower than that of the powders prepared by milling. This is caused by the homogeneous distribution of the additives. The activation energy for the different additives changes in the following sequence: $\Delta E(2\text{BaO}/\text{TiO}_2/2\text{SiO}_2) < \Delta E(\text{TiO}_2) < \Delta E(\text{CaO}/\text{TiO}_2/\text{SiO}_2) < \Delta E(\text{TiO}_2/\text{SiO}_2)$. This sequence correlates with the amount of Ba ions necessary to diffuse out of the BaTiO₃ matrix to form the secondary phases Ba₂TiSi₂O₈ or Ba₆Ti₁₇O₄₀, respectively.

Acknowledgements

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