Ca-containing additives in PTC-BaTiO$_3$ ceramics: effects on the microstructural evolution

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Abstract

Two series of Ca$^{2+}$-modified BaTiO$_3$ ceramics have been prepared of the gross composition La$_{0.002}$Ba$_{0.998}$$_x$Ca$_x$Ti$_{1.01}$O$_{3.02}$ ($0 < x < 0.24$). In the first series, CaCO$_3$, BaCO$_3$, TiO$_2$ and La$_2$(C$_2$O$_4$)$_3$.9H$_2$O were used as starting materials. The calcination of mixtures with $x \leq 0.08$ resulted in the formation of the corresponding titanate solid solution (Ba$_{1-x}$Ca$_x$)TiO$_3$. With values of $x$ higher than 0.08, CaTiO$_3$ was observed as an additional phase. In the second series, a La$_{0.002}$Ba$_{0.998}$TiO$_3$ starting powder was hydrothermally recrystallized in Ca(NO$_3$)$_2$ solution. High resolution imaging and analytical methods revealed that the BaTiO$_3$ grains are surrounded by small CaTiO$_3$ crystallites, which influence the evolution of the microstructure of the ceramic in the sintering process strongly by acting as seeds during the recrystallization of the matrix material. Thus, it was possible to optimize the microstructural and electrical characteristics of a ceramic of the second series by adding only 4 mol% Ca, while in case of the first series 16 mol% Ca are necessary.

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1. Introduction

Barium titanate (BaTiO$_3$) ceramics have attained great industrial importance and a wide application as capacitor materials and PTC (positive coefficient of temperature) devices where BaTiO$_3$ is not used as a pure substance itself. Various substances are usually added to optimize the properties of the ceramic in certain respects. One element frequently used as an additive is calcium. The effect of calcium-containing additives in BaTiO$_3$ ceramics is being discussed controversially in literature, which, on the one hand, is due to the different fields of application, and on the other hand, to the various Ca sources used, and the various modes of adding of the Ca-containing additives during the ceramic processing. If Ca-containing additives are used for the BaTiO$_3$ mixture to be applied as capacitor materials, the matter has been discussed rather unanimously over the last few years.$^{1-5}$ This application requires a high stability of the ceramic in a reducing atmosphere as the inner electrodes to be used are intended to be of cheap nickel metal. The use of Ca-containing additives for this purpose is given if a molar ratio A/B > 1 is realized in the gross composition of the perovskite-type (ABO$_3$) ceramics. Under this condition, Ca$^{2+}$ ions are built in on Ti-sites, yielding Ca$_{Ti}^{0.5}$, despite the fact that the Ca$^{2+}$ ion is 1.5 times bigger than the Ti$^{4+}$ ion, forming Ba(Ca$_{x}$Ti$_{1-x}$)O$_{3-x}$. The solubility limit for Ca$_{Ti}^{0.5}$ is at 2–3 mol%.$^{1,5}$ In addition, a separate phase Ba$_3$Ca$_2$Ti$_2$O$_9$ forms at the grain boundaries in BaTiO$_3$ ceramics having A-sites in excess, thus inhibiting the grain growth.$^5$

\[
\begin{align*}
\text{xCaO} + \text{BaO} + (1 - x)\text{TiO}_2 & \rightarrow \text{Ba}_x\text{Ca}_{x} \text{TiO}_3 \\
+ (x + 1)\text{Ti}_x + (3 - x)\text{O}_x + x\text{V}_o & \text{ (1)}
\end{align*}
\]

The formation of oxygen defects $V^\circ$ under reducing conditions is favored by the formation of acceptor sites Ca$_{Ti}^{0.5}$, thus stabilizing the whole ceramic. The incorporation of Ca$^{2+}$ ions on Ti-sites described by Eq. (1) could be proven by the shifting of the Curie temperature (in temperature-depending measurements of the relative permittivity)$^6$ and by the high resistivity of these ceramics
under atmospheric as well as under reducing sintering conditions. For a B-site excess, which is typical of the composition of ceramics used as PTC-devices, Ca ions are built in on A-sites Ca_{6-x}Ba_{x}Ti_{17}O_{40}. The solubility limit is then about 23 mol%. The TiO₂ excess causes a eutectic at $T_E = 1346°C$. During the sintering process, which mediates the recrystallization of the matrix material, with a final ceramic forming, showing a minimum grain size of $d \geq 5 \mu m$. The addition of Ca-containing components modifies the eutectic and creates a second liquid phase at 1320°C. Blanchart and Holmes describe the possibilities of adjusting the microstructure and the electrical properties of the ceramic by Ca-containing additives. The extent of adjustability the microstructure by Ca²⁺ ions depends on the amount and the source of the Ca-containing additive.

The most frequently used Ca source is CaCO₃, which as a starting material is used together with BaCO₃ and TiO₂ to produce the ceramic starting powder. Dabrunz varied the Ca²⁺ content accurately by using this method of incorporation. The grain size of the sintered ceramic was decreasing continuously with the Ca content increasing up to 16 mol%. The inhibition of the grain growth is considered the reason for this behavior. Kolar describes a maximum of grain size of the sintered samples at a Ca content of 8 mol%, if Ca is added as CaTiO₃, and if a large excess of TiO₂ is used in form of Ba₆Ti₁₇O₄₀. With a higher Ca content, the Ca-stabilized phase Ba₅Ti₂O₁₂ forms, which is proven to impede the discontinuous grain growth. No characteristics are given of the CaTiO₃ powder added. Tiwari et al. used a separately prepared solid solution (Ba, Ca)CO₃ as the Ca source. There, however, was no indication of a dependence of the grain size of the ceramics sintered at 1300°C on the Ca content.

The mechanism of the formation of titanate solid solution (Ba, Ca)TiO₃ using both (Ba, Ca)CO₃ + TiO₂ and BaCO₃ + CaCO₃ + TiO₂ as starting mixtures has been investigated by Müller. The phases Ba₅Ca₂Ti₂O₉ and CaTiO₃ have been detected as intermediates.

This paper reports on the effect of different Ca-containing additives on the microstructural evolution and the electrical properties of (Ba, Ca)TiO₃-PTC ceramics. Two series of Ca-containing BaTiO₃ ceramics have been prepared differing in the mode of incorporation of the Ca-containing additive into the starting composition. One of the preparation methods (Series “H”) has been described by us only lately.

2. Experimental

The following series of Ca-modified BaTiO₃ ceramics of the gross composition La₀.₀ₐBa₀.₉ₙₓTi₁.₀₁O₃.ₙ₂, with $0 < x < 0.24$, have been prepared.

2.1. Series C (“conventional”)

Via the conventional mixed-oxide method, the starting materials BaCO₃ and CaCO₃ (both from Leuchttstoffe und Feinchemikalien GmbH Bad Liebenstein), TiO₂ (Merck 808) and La₃(C₂O₄)₉.9H₂O (SKW Piestritz) were wet mixed/milled in a ball mill using PTFE-coated steel balls, and distilled water as the milling liquid. After 24 h of milling, the mixture was filtered and the powder was dried. The dried powder was then annealed at 1100°C for 2 h in a corundum crucible before it was milled, filtered and dried, again (average grain size ~1 μm).

2.2. Series H (“hydrothermal”)

A BaTiO₃ starting powder of the composition La₀.₀₂Ba₀.₉₉₈TiO₃ was prepared via the conventional mixed-oxide method described above up to the annealing step. The calcined powder was crushed in a mortar. 20 g of this powder were suspended in 80 cm³ of an aqueous Ca(NO₃)₂ solution of given concentration. The CO₂-free water used was prepared by boiling and flow-through of Argon.

The suspension was hydrothermally treated in a laboratory autoclave (Berghoff HR 200) under autoclave pressure at 180°C and stirring for 24 h. Finally, the suspension was separated by centrifugation. The powder was rinsed with distilled water and dried. The liquid phase was analyzed by atomic absorption flame spectroscopy (Varian Spectra20 instrument).

The as-prepared powders of both series were mixed with 5 mass% poly(vinyl alcohol) solution (mixture of poly(vinyl alcohol), glycerol and water) as a pressing aid for 24 hours. After that, the powders were granulated and pressed into pellets (12 mm diameter, 2 mm thick) of about 3.1 g/cm³ in density. These greens were heated up to 750°C at a rate of 5 K/min ensuring the complete burning-out of the pressing aid, before they were sintered at a heating rate of 10 K/min up to the sintering temperature $T_S = 1350°C$ in air using a corundum crucible with ZrO₂ powder as support. The dwelling time at $T_S$ was usually 1 h. After that the samples were cooled down to 800°C at a rate of 10 K/min. The sinters were polished and chemically etched to investigate the microstructure. The grain size was determined using the linear intercept method.

For testing the electrical resistance at room temperature, the front faces of the sintered pellets were coated with Ga-In eutectic electrodes to provide ohmic contacts. The electrical resistivity was calculated from the voltage $U$ (0.1 V) and the current intensity $I$ values at 22°C, and the geometric parameters of the sample. The voltage withstanding E was ascertained as the voltage value at the I-minimum in the $I–U$ plot, and correlated to the thickness of the pellet.
For electron probe microanalysis (EPMA), the polished samples were additionally vapour-deposited with carbon. The element distribution was determined by wave length dispersive X-ray spectrometry (Camebax, Cameca Co., France). BaTiO₃ and CaTiO₃ single crystals were used as reference samples.

For the TEM/STEM investigations, the different sets of specimens were prepared by dispersing a small amount of the powder in pure ethanol, mixing it in an ultrasonic generator, and pipetting a drop of this dispersion on a copper mesh covered with a perforated carbon film. To minimize the contamination effects during analyses, which are generally strong for electron probes as small as some nanometres, the specimen grid was kept at the liquid-nitrogen temperature via a cooling specimen holder (Gatan, type 668).

Electron energy loss spectroscopy (EELS) was applied using a parallel-recording spectrometer (PEELS, Gatan GIF 200, type 678, ca. 0.8–1.2 eV energy resolution) attached to a TEM/STEM Philips CM 20 FEG instrument run at 200 keV. Point analyses were recorded in the STEM mode, using an electron probe of 2 nm diameter.

3. Results and discussion

3.1. Characterization of the prepared powders

The Ca content of the samples was changed by varying the amount of CaCO₃ to be added (series C) or by varying the concentration of the Ca(NO₃)₂ solution (series H).

The processes during the calcination of the mixtures of series C investigated by Müller et al.¹⁵ proved that at a calcination temperature of 1100°C, the titanate solid solution (Ba₁₋ₓCaₓ)TiO₃ forms from the corresponding mixture (1₋ₓ)BaCO₃ + xCaCO₃ + TiO₂ for x ≤ 0.08. For larger values of x, CaTiO₃ appears as an additional, separate phase. Only at temperatures T > 1200°C and under equilibrium conditions these separate phases, (Ba₀.₉₂Ca₀.₀₈)TiO₃ and CaTiO₃, form the titanate solid solution (Ba₁₋ₓCaₓ)TiO₃ with values of x corresponding to the starting molar Ba/Ca ratio.

The deliberate exploitation of the different thermodynamic stability of BaTiO₃ and CaTiO₃ in aqueous environment makes it possible to modify the surface of BaTiO₃ particles with CaTiO₃ crystallites.¹⁶ For series H (Fig. 1), under the given reaction conditions the Ca-modification process is thermodynamically controlled. 95–98% of the Ca ions solved in the liquid phase are transferred into the solid phase CaTiO₃. On the other hand, the Ba²⁺ amount dissolved from the BaTiO₃ starting powder into the liquid phase is 0.5 to 1 mol% higher than the solidified Ca²⁺ amount (all related to the amount of substance of the BaTiO₃ starting powder). This difference corresponds to the dissolved Ba²⁺ amount under the same hydrothermal leaching conditions in pure water (0.68 mol%).

These results show that by varying the amount of Ca²⁺ ions in the leaching liquid under hydrothermal conditions, it is possible to prepare BaTiO₃ powders with a certain amount of CaTiO₃ additive and a defined excess of TiO₂.

The morphology of such a hydrothermally modified BaTiO₃ powder is shown in Fig. 2 containing 16 mol%...
CaTiO₃. The surfaces of the BaTiO₃ particles are coated with cuboid CaTiO₃ crystallites of 20 to 100 nm in size. The mechanism of the formation of these structures can be described as a combined dissolution/recrystallization process. The complete dissolution of the surface layers of the original BaTiO₃ grains of the starting powder is followed by the heterogeneous crystallization of the CaTiO₃ particles on the surface of the BaTiO₃ grains.

Increasing the concentration of the Ca(NO₃)₂ solution will increase the number of CaTiO₃ crystallites, the crystallite size, however, not changing.

3.2. Effects on the microstructure and electrical properties of the ceramics

The effect of varying the Ca content on the microstructure is demonstrated in Fig. 3 for both series of ceramics sintered at 1350°C. A content of only 2 mol% CaTiO₃ in series H decreases the average grain size of the ceramics, sintered at 1350°C significantly from 43 μm for the Ca-free, but hydrothermal modified BaTiO₃ starting powder to 20 μm. For a Ca content of 4 mol%, the average grain size is 8.3 μm, and for 8 mol% it is 4.8 μm. For the ceramics of series C, the average grain size of 10 μm, which is reasonably good for PTC application, is reached only if the Ca content is higher than 12 mol%.

The electrical characteristics (voltage withstanding E and resistivity at room temperature ρ₂⁰) of Ca-modified ceramics of both series are summarized in Table 1 demonstrating that using CaCO₃ as Ca source (series C) will markedly increase the voltage withstanding of the ceramic to 60 V/mm only if the Ca content is 12–16 mol%. For a ceramic prepared via hydrothermal Ca-modification (series H), this value of E is reached with only 4 mol% Ca.

The resistivity/temperature measurements of ceramics with x = 0.04 exhibit a steeper slope of resistivity above the Curie temperature in series H. The resistivity jump is 3.4 orders of magnitude within 90–245°C, compared to 2.9 orders of magnitude within 90–290°C for ceramics of series C.

These results clearly show that the mode chosen of incorporating Ca-containing additives influences the
microstructure and the electrical properties of the final ceramics considerably. The differences in the properties are due to the different mechanisms of the Ca additives operative during the sintering process. These mechanisms have been elucidated by microstructural and microanalytical investigations of the ceramics using EPMA and electron energy loss spectroscopy (EELS). Fig. 4 shows the microstructure of the ceramic of the gross composition La$_{0.002}$Ba$_{0.958}$Ca$_{0.04}$Ti$_{1.01}$O$_{3.02}$ after hydrothermal modification (series H), and the corresponding Ca-mapping image. The cores of the grains clearly show Ca enrichments marked by x. The analysis of the series-C ceramic of the same gross composition shows, however, a homogeneous Ca-distribution.

Two other ceramics with an effective composition La$_{0.002}$Ba$_{0.998}$Ca$_{0.04}$Ti$_{1.01}$O$_{3.02}$ were prepared by mixing a La$_{0.002}$Ba$_{0.998}$TiO$_3$ starting powder with CaCO$_3$ + TiO$_2$, and with separately prepared CaTiO$_3$, respectively. Both ceramics were also enriched in Ca in the cores of their grains (Fig. 5).

These results imply the following mechanism during sintering of BaTiO$_3$ ceramics with Ca-containing additives: If there are individual CaTiO$_3$ crystallites in the ceramic starting powder before sintering, they will act as seeds during the recrystallization of the matrix material. As the sintering proceeds far away from the thermodynamic equilibrium the Ca concentration is not uniform in the sample at temperatures below the eutectic temperature of 1346°C. Ca inhomogeneities have been proven by EELS in powders of series H with 4 mol% Ca even at 1300°C. Annealing at this temperature for 2 h changes the structure and the composition of the CaTiO$_3$ crystallites surrounding the BaTiO$_3$ particles. Thus, the EELS measurements (Fig. 6) indicate that the big particles in the middle are still pure barium titanate. They are, however, surrounded now by a titanate solid solution (Ba,Ca)TiO$_3$ with a Ca content of 6 mol%. This change results from diffusion processes between the original central particle and the surrounding CaTiO$_3$ crystallites. The preference of the Ba$^{2+}$ diffusion is surprising. Ca ions occur solely in the surrounding (Ba,Ca)TiO$_3$ crystallites (originally CaTiO$_3$), but not in the big central particles.

Butler et al.$^{18}$ describe similar observations pointing out that the diffusion coefficient $D$ of Sr$^{2+}$ ions in CaTiO$_3$ is larger than that of Ca$^{2+}$ ions in SrTiO$_3$, and that $D_{Ba}$ (in SrTiO$_3$) is greater than $D_{Sr}$ (in BaTiO$_3$). They explain this by the easier formation and the larger number of A-site vacancies $V_A^{Ca}$ in CaTiO$_3$ compared to BaTiO$_3$.

As sintering proceeds at a high heating rate, the phase state before the recrystallization via the eutectic melt is described more realistically by the coexistence of CaTiO$_3$ and BaTiO$_3$ crystallites.

In series C, CaTiO$_3$ crystallites can be detected solely in compositions with a Ca content higher than 8 mol% influencing the recrystallization of the matrix material in the same way as in series H. Hence, the significant changes in the microstructure of the ceramics in the range of 8 to 10 mol% Ca (Fig. 3), and the similarities of the properties of the ceramics of series C with 12 to 16 mol% Ca to those of series H with 4 mol% Ca are easy to understand.

### Table 1

<table>
<thead>
<tr>
<th>Series C</th>
<th>Series H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca content $x$ (mol%)</td>
<td>$E$ (V/mm)</td>
</tr>
<tr>
<td>4</td>
<td>8.4</td>
</tr>
<tr>
<td>8</td>
<td>11.2</td>
</tr>
<tr>
<td>12</td>
<td>44.2</td>
</tr>
<tr>
<td>16</td>
<td>60.5</td>
</tr>
</tbody>
</table>

Fig. 4. Microstructure of a ceramic of composition La$_{0.002}$Ba$_{0.998}$Ca$_{0.04}$Ti$_{1.01}$O$_{3.02}$ (series H), sintered at 1350°C, investigated by EPMA: left, SE image; right, Ca distribution.
EPMA investigation of the ceramic of series C with 16 mol% Ca sintered at 1350°C show Ca segregations as well, however, located mainly near the grain boundaries but not unambiguously within the grains.

Therefore, Ca additives in BaTiO₃ ceramic starting powders in the series investigated should be considered not grain-growth to inhibit, but to influence nucleation, with the CaTiO₃ crystallites acting as seeds.

Comparing the tendencies of the microstructural and electrical characteristics of the ceramics shows that the major changes in the electrical properties as a function of the Ca content correlate with changes in the microstructure. The conversion of the values of the voltage withstanding and the electrical resistance of the ceramics into values of the single grains yielded similar results (e.g. 0.25 V/grain boundary) for all ceramics.

4. Conclusions

Two series of Ca²⁺-modified barium titanate ceramics La₀.₀₀₂Ba₀.₉₉₈₋ₓCaₓTi₁₀₁₋ₙO₃₃ were prepared and investigated. The first one (“C”) was manufactured using CaCO₃ as the Ca source via the conventional mixed-oxide method. At a calcination temperature of 1100°C, the mixtures (1–x) BaCO₃ + x CaCO₃ + TiO₂

Fig. 5. Microstructure of a ceramic of composition La₀.₀₀₂Ba₀.₉₉₈₋ₓCaₓTi₁₀₁₋ₙO₃₃, prepared via mixed-oxide method using La₀.₀₀₂Ba₀.₉₉₈₋ₓCaₓTi₁₀₁₋ₙO₃₃ as starting materials, sintered at 1350°C, investigated by EPMA: left, SE image; right, Ca distribution.

Fig. 6. EEL spectra of a BaTiO₃ central grain (upper spectrum) and of the peripheral (Ba₁₋ₓCaₓ)TiO₃ surroundings (lower spectrum) of a powder of series H (4 mol% Ca) after annealing at 1300°C.
with $x \leq 0.08$ form the corresponding titanate solid solution ($\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$). For higher values of $x$, CaTiO$_3$ has been detected as an additional, separate phase.

In the second series, ("H"), a La$_{0.002}$Ba$_{0.998}$TiO$_3$ starting powder was hydrothermally modified in a Ca(NO$_3$)$_2$ solution. This hydrothermal modification turns out to be a thermodynamically controlled recrystallization process, yielding BaTiO$_3$ particles surrounded by CaTiO$_3$ crystallites. These CaTiO$_3$ crystallites strongly influence the evolution of the microstructure during sintering and therefore also the electrical properties of the ceramic. The CaTiO$_3$ crystallites were found to act as seeds during the recrystallization of the matrix material. Knowing this mechanism of the CaTiO$_3$ additives during the sintering of the matrix material. Knowing this mechanism of the CaTiO$_3$ additives during the sintering of the matrix material. Knowing this mechanism of the CaTiO$_3$ additives during the sintering of the matrix material.

Acknowledgements

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