

Ca-containing additives in PTC-BaTiO₃ ceramics: effects on the microstructural evolution

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Abstract

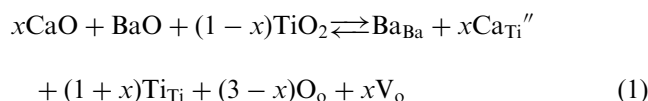
Two series of Ca²⁺-modified BaTiO₃ ceramics have been prepared of the gross composition La_{0.002}Ba_{0.998-x}Ca_xTi_{1.01}O_{3.02} (0 < x < 0.24). In the first series, CaCO₃, BaCO₃, TiO₂ and La₂(C₂O₄)₃·9H₂O were used as starting materials. The calcination of mixtures with x ≤ 0.08 resulted in the formation of the corresponding titanate solid solution (Ba_{1-x}Ca_x)TiO₃. With values of x higher than 0.08, CaTiO₃ was observed as an additional phase. In the second series, a La_{0.002}Ba_{0.998}TiO₃ starting powder was hydrothermally recrystallized in Ca(NO₃)₂ solution. High resolution imaging and analytical methods revealed that the BaTiO₃ grains are surrounded by small CaTiO₃ 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. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Barium titanate (BaTiO₃) ceramics have attained great industrial importance and a wide application as capacitor materials and PTC (positive coefficient of temperature) devices where BaTiO₃ 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 BaTiO₃ 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 BaTiO₃ 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 (ABO₃) ceramics. Under this condition, Ca²⁺ ions are built in on Ti-sites, yielding Ca_{Ti}^{''}, despite the fact that the Ca²⁺ ion is 1.5 times bigger than the Ti⁴⁺ ion, forming Ba(Ca_xTi_{1-x})O_{3-x}. The solubility limit for Ca_{Ti}^{''} is at 2–3 mol%.^{1,5} In addition, a separate phase Ba₃Ca₂Ti₂O₉ forms at the grain boundaries in BaTiO₃ ceramics having A-sites in excess, thus inhibiting the grain growth.⁵



The formation of oxygen defects V_o^\bullet under reducing conditions is favored by the formation of acceptor sites Ca_{Ti}^{''}, thus stabilizing the whole ceramic. The incorporation of Ca²⁺ 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)⁴ and by the high resistivity of these ceramics

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under atmospheric as well as under reducing sintering conditions.⁶

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_{Ba}^x , $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$. The solubility limit is then about 23 mol%.⁷ The TiO_2 excess causes a eutectic at $T_E = 1346^\circ\text{C}$.⁸ during the sintering process, which mediates the recrystallization of the matrix material, with a final ceramic forming, showing a minimum grain size of $d \geq 5 \mu\text{m}$. The addition of Ca-containing components modifies the eutectic and creates a second liquid phase at 1320°C .⁹ Blanchart¹⁰ and Holmes¹¹ 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 Ca^{2+} ions depends on the amount and the source of the Ca-containing additive.

The most frequently used Ca source is CaCO_3 , which as a starting material is used together with BaCO_3 and TiO_2 to produce the ceramic starting powder.^{10–12} Dabrunz¹² varied the Ca^{2+} 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.¹⁰

Kolar¹³ describes a maximum of grain size of the sintered samples at a Ca content of 8 mol%, if Ca is added as CaTiO_3 , and if a large excess of TiO_2 is used in form of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$. With a higher Ca content, the Ca-stabilized phase $\text{Ba}_2\text{Ti}_5\text{O}_{12}$ forms, which is proven to impede the discontinuous grain growth. No characteristics are given of the CaTiO_3 powder added. Tiwari et al.¹⁴ used a separately prepared solid solution $(\text{Ba,Ca})\text{CO}_3$ 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 $(\text{Ba,Ca})\text{TiO}_3$ using both $(\text{Ba,Ca})\text{CO}_3 + \text{TiO}_2$ and $\text{BaCO}_3 + \text{CaCO}_3 + \text{TiO}_2$ as starting mixtures has been investigated by Müller.¹⁵ The phases $\text{Ba}_3\text{Ca}_2\text{Ti}_2\text{O}_9$ and CaTiO_3 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 $(\text{Ba,Ca})\text{TiO}_3$ -PTC ceramics. Two series of Ca-containing BaTiO_3 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.¹⁶

2. Experimental

The following series of Ca-modified BaTiO_3 ceramics of the gross composition $\text{La}_{0.002}\text{Ba}_{0.998-x}\text{Ca}_x\text{Ti}_{1.01}\text{O}_{3.02}$, with $0 < x < 0.24$, have been prepared.

2.1. Series C (“conventional”)

Via the conventional mixed-oxide method, the starting materials BaCO_3 and CaCO_3 (both from Leuchtstoffe und Feinchemikalien GmbH Bad Liebenstein), TiO_2 (Merck 808) and $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ (SKW Piesteritz) 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 $\sim 1 \mu\text{m}$).

2.2. Series H (“hydrothermal”)

A BaTiO_3 starting powder of the composition $\text{La}_{0.002}\text{Ba}_{0.998}\text{TiO}_3$ 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 cm^3 of an aqueous $\text{Ca}(\text{NO}_3)_2$ solution of given concentration. The CO_2 -free water used was prepared by boiling and flowing-through of Argon.

The suspension was hydrothermally treated in a laboratory autoclave (Berghoff HR 200) under autogeneous 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/cm^3 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 $T_S = 1350^\circ\text{C}$ in air using a corundum crucible with ZrO_2 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). BaTiO_3 and CaTiO_3 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 CaCO_3 to be added (series C) or by varying the concentration of the $\text{Ca}(\text{NO}_3)_2$ 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 $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$ forms from the corresponding mixture $(1-x)\text{BaCO}_3 + x\text{CaCO}_3 + \text{TiO}_2$ for $x \leq 0.08$. For larger values of x , CaTiO_3 appears as an additional, separate phase. Only at temperatures $T > 1200^\circ\text{C}$ and under equilibrium conditions these separate phases, $(\text{Ba}_{0.92}\text{Ca}_{0.08})\text{TiO}_3$ and CaTiO_3 , form the titanate solid solution $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$ with values of x corresponding to the starting molar Ba/Ca ratio.

The deliberate exploitation of the different thermodynamic stability of BaTiO_3 and CaTiO_3 in aqueous environment makes it possible to modify the surface of BaTiO_3 particles with CaTiO_3 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 CaTiO_3 . On the other hand, the Ba^{2+} amount dissolved from the BaTiO_3 starting powder into the liquid phase is 0.5 to 1 mol% higher than the solidified Ca^{2+} amount (all related to the amount of substance of the BaTiO_3 starting powder). This difference corresponds to the dissolved Ba^{2+} amount under the same hydrothermal leaching conditions in pure water (0.68 mol%).

These results show that by varying the amount of Ca^{2+} ions in the leaching liquid under hydrothermal conditions, it is possible to prepare BaTiO_3 powders with a certain amount of CaTiO_3 additive and a defined excess of TiO_2 .

The morphology of such a hydrothermally modified BaTiO_3 powder is shown in Fig. 2 containing 16 mol%

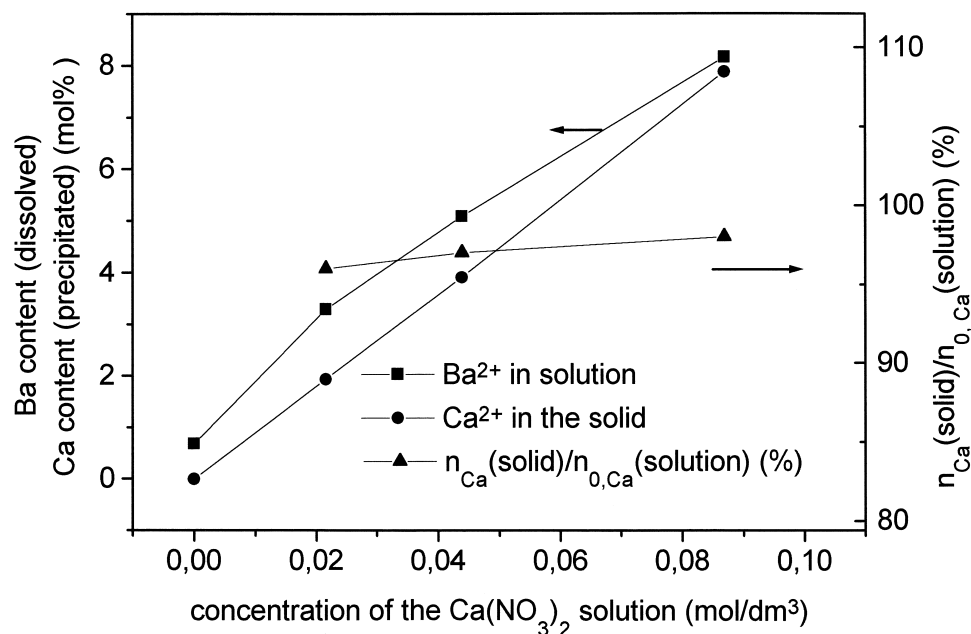


Fig. 1. Dissolved Ba^{2+} and incorporated Ca^{2+} content, respectively, of the BaTiO_3 starting powder after hydrothermal modification in a $\text{Ca}(\text{NO}_3)_2$ solution of different concentration.

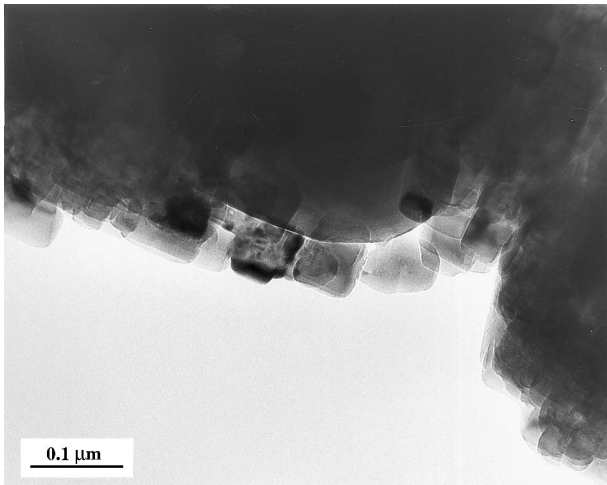


Fig. 2. Typical morphology of the BaTiO_3 starting powder hydrothermally modified in a $\text{Ca}(\text{NO}_3)_2$ solution: TEM dark-field image of a BaTiO_3 grain surrounded by cuboid CaTiO_3 crystallites.

CaTiO_3 . The surfaces of the BaTiO_3 particles are coated with cuboid CaTiO_3 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.¹⁶ The complete dissolution of the surface layers of the original BaTiO_3 grains of the starting powder is followed by the heterogeneous crystallization of the CaTiO_3 particles on the surface of the BaTiO_3 grains.

Increasing the concentration of the $\text{Ca}(\text{NO}_3)_2$ solution will increase the number of CaTiO_3 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% CaTiO_3 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 BaTiO_3 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 contents higher than 12 mol%.

The electrical characteristics (voltage withstanding E and resistivity at room temperature ρ_{20}) of Ca-modified ceramics of both series are summarized in Table 1 demonstrating that using CaCO_3 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 $90\text{--}245^\circ\text{C}$, compared to 2.9 orders of magnitude within $90\text{--}290^\circ\text{C}$ for ceramics of series C.

These results clearly show that the mode chosen of incorporating Ca-containing additives influences the

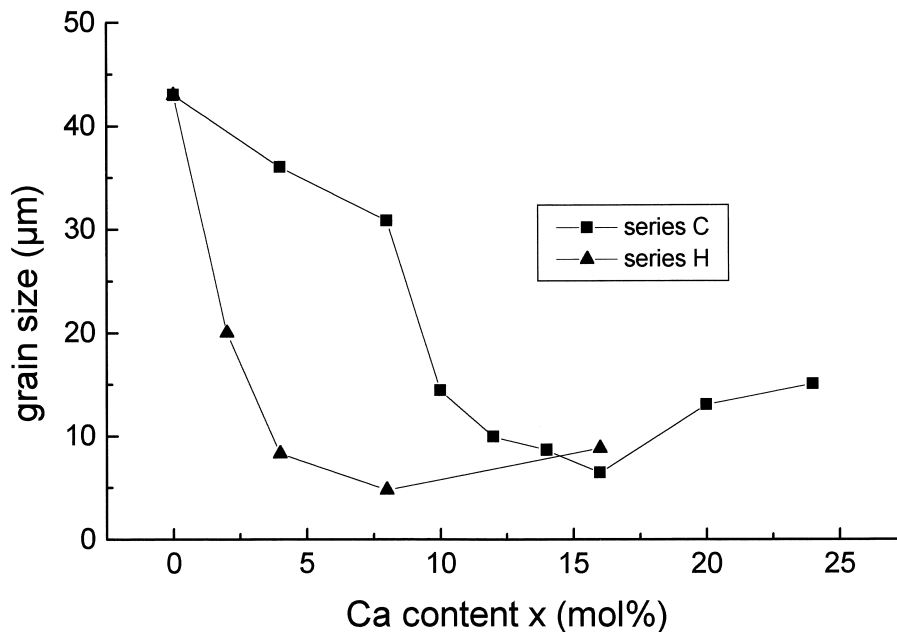


Fig. 3. Influence of the Ca content on the grain size of the final ceramic $\text{La}_{0.002}\text{Ba}_{0.998-x}\text{Ca}_x\text{Ti}_{1.01}\text{O}_{3.02}$, with Ca incorporated from CaCO_3 via mixed-oxide method (series C) and from CaTiO_3 via hydrothermal modification (series H) (sintering temperature 1350°C).

Table 1
Voltage withstanding E and resistivity at room temperature ρ_{20} of Ca-modified ceramics, $\text{La}_{0.002}\text{Ba}_{0.998-x}\text{Ca}_x\text{Ti}_{1.01}\text{O}_{3.02}$, sintered at 1350°C

Series C			Series H		
Ca content x (mol%)	E (V/mm)	ρ_{20} (Ωcm)	Ca content x (mol%)	E (V/mm)	ρ_{20} (Ωcm)
4	8.4	17.8	0	14.3	15.3
8	11.2	20.9	4	58.5	174
12	44.2	41.1	8	68.4	342.6
16	60.5	892	16	32.4	48.8

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 $\text{La}_{0.002}\text{Ba}_{0.958}\text{Ca}_{0.04}\text{Ti}_{1.01}\text{O}_{3.02}$ 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 $\text{La}_{0.002}\text{Ba}_{0.958}\text{Ca}_{0.04}\text{Ti}_{1.01}\text{O}_{3.02}$ were prepared by mixing a $\text{La}_{0.002}\text{Ba}_{0.998}\text{TiO}_3$ starting powder with $\text{CaCO}_3 + \text{TiO}_2$, and with separately prepared CaTiO_3 ,¹⁷ 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 $(\text{Ba,Ca})\text{TiO}_3$ 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 $(\text{Ba,Ca})\text{TiO}_3$ 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}'' 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.

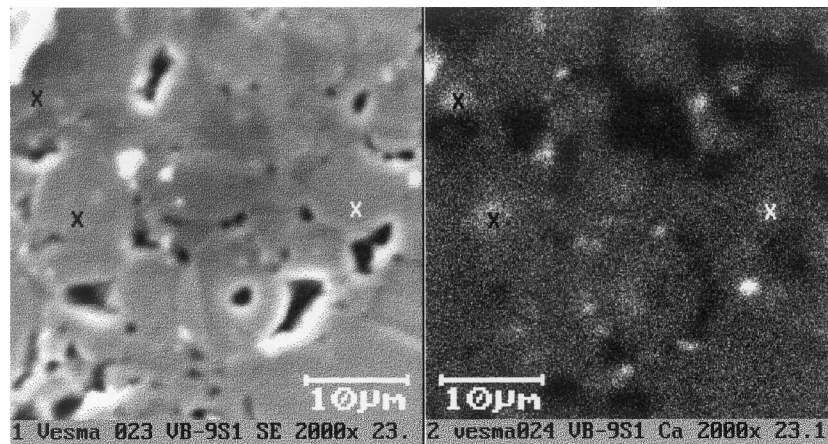


Fig. 4. Microstructure of a ceramic of composition $\text{La}_{0.002}\text{Ba}_{0.958}\text{Ca}_{0.04}\text{Ti}_{1+x}\text{O}_{3+2x}$, (series H), sintered at 1350°C , investigated by EPMA: left, SE image; right, Ca distribution.

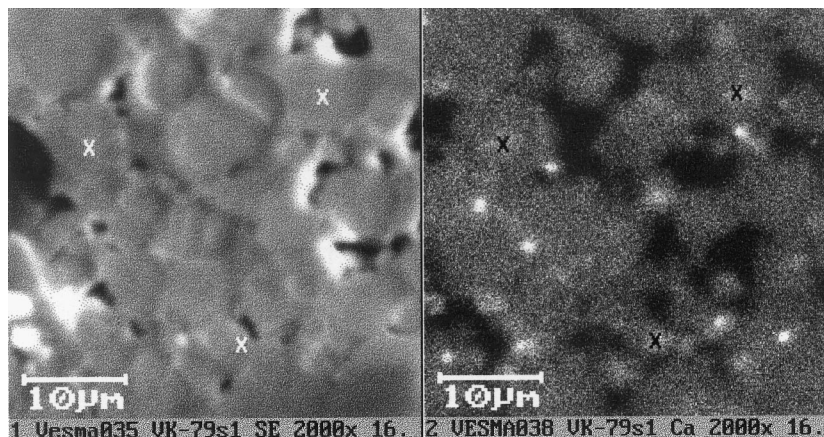


Fig. 5. Microstructure of a ceramic of composition $\text{La}_{0.002}\text{Ba}_{0.958}\text{Ca}_{0.04}\text{Ti}_{1+x}\text{O}_{3+2x}$, prepared via mixed-oxide method using $\text{La}_{0.002}\text{Ba}_{0.998}\text{TiO}_3 + (\text{CaCO}_3 + \text{TiO}_2)$ as starting materials, sintered at 1350°C , investigated by EPMA: left, SE image; right, Ca distribution.

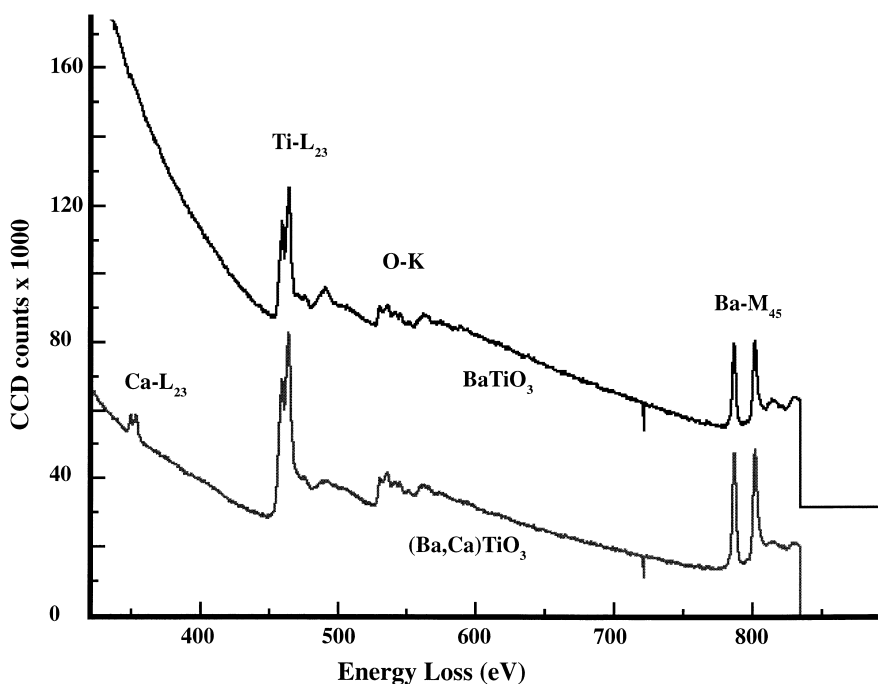


Fig. 6. EEL spectra of a BaTiO_3 central grain (upper spectrum) and of the peripheral $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$ surroundings (lower spectrum) of a powder of series H (4 mol% Ca) after annealing at 1300°C .

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 BaTiO_3 ceramic starting powders in the series investigated should be considered not grain-growth to inhibit, but to influence nucleation, with the CaTiO_3 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 Ca^{2+} -modified barium titanate ceramics $\text{La}_{0.002}\text{Ba}_{0.998-x}\text{Ca}_x\text{Ti}_{1.01}\text{O}_{3.02}$ were prepared and investigated. The first one ("C") was manufactured using CaCO_3 as the Ca source via the conventional mixed-oxide method. At a calcination temperature of 1100°C , the mixtures $(1-x)\text{BaCO}_3 + x\text{CaCO}_3 + \text{TiO}_2$

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 $\text{La}_{0.002}\text{Ba}_{0.998}\text{TiO}_3$ starting powder was hydrothermally modified in a $\text{Ca}(\text{NO}_3)_2$ 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 process enables one to develop a ceramic with a CaTiO_3 content of 4 mol% and with microstructural and electrical characteristics comparable to those of a ceramic with 16 mol% Ca prepared via mixed-oxide method.

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