INTRODUCTION

Semiconducting titanates like BaTiO$_3$ (BTO), SrTiO$_3$ (STO), and Sr$_x$Ba$_{1-x}$TiO$_3$ (BST) ($0 \leq x \leq 1$) show interesting applications in electronics and communication technology due to their high dielectric constant. By substituting Sr with Ba in the lattice position of alkaline earth elements, the cubic perovskite crystallographic structure changes into a tetragonal one due to the larger ionic radius of barium ion, which is inducing a change in physical properties, that is, the positive temperature coefficient of resistivity. Additionally, the properties of this class of materials can be strongly influenced by doping with different elements like Nb, La, Fe, Mn, Ce etc. BTO is used in piezoelectric devices like loudspeaker and ultrasonic transducers. STO is used in gas sensors in harsh environments and for thermoelectric energy conversion, just to mention a few examples.

Common synthesis routes for synthesis of Ba/Sr titanates are solid-state and sol-gel methods. The solid-state method often uses barium and strontium carbonates, titanium dioxide, and the desired doping elements in oxidic form, which are mixed, subsequently ball milled, and calcined. A very
high purity of the final product can be achieved using pure and high-quality raw materials in powder form. The powders need to be very fine to achieve high reactivity. Complete miscibility needs to be guaranteed to obtain the desired stoichiometric ratio. Due to the ball milling step, the synthesis of core-shell particles is not compatible with the solid-state route as the architecture of the substrate and the oxide shell will be destroyed.

Sol-gel synthesis uses, for example, barium and strontium acetate and tetrabutyl titanate as precursors. After hydrolysis and gelation, the intermediate is dried and calcined to obtain the final product. Nanoparticular structures can be obtained by the deposition of thin films and ceramic nanopowders can be produced. Precursors and suitable reagents for the use as dopant (eg, Niobium(V) ethoxide or -isopropoxide) are expensive in large-scale production and the overall volume yield is very low due to the high dissolution factors.

Wet-chemical precipitation from salt solutions has the advantage that the synthesis of core-shell particles is possible. The core-shell terminology used in this study should not be confused with the commonly used concept of it where in a single grain ceramic, the outer layer of the grain has a slightly different composition. The change in pH and temperature initiates the precipitation and the Al₂O₃ flakes are coated with a ceramic material in the composition BaTiO₃ or SrTiO₃ doped with different elements like Nb, Mn, or Ce. The core particles have sizes between 10 and 30 µm and determine the geometry of the resulting product. Al₂O₃ flakes are suitable because of their high-temperature stability and smooth surfaces. They have a defined crystallographic structure and X-ray diffraction (XRD) diffractograms are easy to evaluate.

By changing key parameters, such as dispense rate (precursor concentration), pH, and temperature, the synthesis can be controlled and the properties of the final product can be influenced. A calcination step after filtration, washing, and drying of the precipitated product forces the conversion of loosely precipitated hydroxides into dense structured oxides around the substrate. Defined electrical properties can be achieved as the electric resistivity is lower within a grain and higher at grain boundaries. As precipitation is outperformed in aqueous medium, counterions—especially halides—can act as impurities and influence the calcination process. Beneficial is that the precursors are cheap and the absence of carbon (compared to sol-gel method with organic components) during the whole process is favorable for controllable electrical resistance.

The materials described in this study show nonlinear electric behavior. A schematic drawing of the general characteristic is illustrated in Figure 1.

The characteristic curve can be described by the following equation, which significantly differs from the classical ohmic equation by the introduction of the nonlinear exponent α:

\[ R = U^\alpha / I \]

\[ \alpha = \begin{cases} 1: \text{classical ohmic equation} \\ \alpha > 1: \text{electrical field–dependent nonlinear conductive behavior} \end{cases} \]

where \( R \) is the resistivity, \( U \) is the voltage, \( I \) is the current, and \( \alpha \) is the nonlinearity coefficient.

For better comparison between different sample geometries, electric current and voltage are converted into normalized values using DC electric field strength \( E \) and current density \( J \).

The nonlinearity coefficient \( \alpha \) is determined by fitting the middle region of the double-logarithmic EJ curve in Figure 1 with a straight line and calculating the slope using two points \(- (E_1, J_1) \) and \( (E_2, J_2) \) - via the formula shown in the inset.

The electrical characteristics of the silicone composite filled with the synthesized ceramic microparticles are determined by measuring the electric current for increasing voltages.

Devices which make use of the nonlinear electric behavior are called varistors (variable resistor) and are used to protect electrical circuits from voltage surges. They act as a back-to-back Zener diode: The varistor becomes conductive when the voltage exceeds the threshold voltage and gets the attached part grounded. The varistor returns to its normal functionality in a highly resistive state when the voltage is lower than the threshold voltage.

For a very long time, zinc oxide (ZnO) has been known to have such properties and has been further developed ever since. One disadvantage of ZnO is the low dielectric constant, which results in a reduced energy absorption. This is the reason for research on doped TiO₂ and Ba/SrTiO₃ to achieve similar electric behavior.

Using powder materials with varistor characteristics as fillers in an insulating polymer matrix, the composite will show nonlinear electric properties as well. The nonlinearity coefficient of such composites should not be as high as...
ceramic bulk varistors (with $\alpha = 20-100$) because high current density would lead to thermal decomposition of the polymer. Commercially available are ZnO microvaristors with $\alpha$ up to 20\textsuperscript{33} and a high density.\textsuperscript{34} This leads to an inhomogeneous distribution of the filler in a silicone matrix as the particles settle down while the resin is cross-linking, which is causing uncontrollable electrical properties.\textsuperscript{35} Using the previously described core-shell approach having a low-density core, it is possible to synthesize fillers with similar electrical characteristics without inhomogeneous distribution.

2 | EXPERIMENTAL PROCEDURE

The synthesis is based on a modified peroxide route described in literature.\textsuperscript{36,37} The experimental setup consists of a double-walled reactor in which temperature, agitator speed, and pH are controlled via a computer. In a typical synthesis, 100 g ($\alpha$-)Al$_2$O$_3$ flakes (Merck) having particle sizes between 10 and 30 µm are suspended in 2 L of purified water (DI-water). The suspension is stirred with a blade agitator at 1000 rpm during the whole process. The temperature of the solution is set to 10°C using a cryostat. In a first step, the pH is set to 1.8 using diluted hydrochloric acid (18 wt%). Two different reagent solutions are dispensed with a rate of 2 mL/min. The first solution contains TiCl$_4$ (Merck, 25 wt% in hydrochloric acid), NbCl$_5$ (Aldrich, purity 99%), MnCl$_2$·4H$_2$O (Merck, for analysis), and CeCl$_3$·7H$_2$O (Aldrich, purity 99.9%) dissolved in hydrochloric acid. The second one contains SrCl$_2$·6H$_2$O (Merck, purity 99%), BaCl$_2$·2H$_2$O (Merck, purity 99%), purified water, and H$_2$O$_2$ (Merck, 30 wt%). The reagent solutions are calculated stoichiometrically to form the final product BaTiO$_3$ and SrTiO$_3$. The amount of doping elements Nb, Mn, and Ce is calculated with the assumption that they substitute Ti-lattice positions, which then results in a slightly smaller amount of titanium. The prepared compositions for different investigation methods with calculated amount of dopants are summarized in Table 1.

Table 1: Prepared compositions with calculated amounts of desired dopants for different investigation methods used in this study

| Investigation                  | Titinate       | Doping            |
|-------------------------------|----------------|-------------------|
|                               | BTO/STO        | Ti                | Nb       | Mn       | Ce       |
| TEM                           | SrTiO$_3$      |                  | 2.0 mol% | —        | —        |
|                               | 187.97 g       | 56.48 g TiCl$_4$ | 31.75 g  |          |          |
|                               | SrCl$_2$·6H$_2$O |                  |          |          |          |
|                               | 2.0 mol%       |                  |          |          |          |
|                               | NbCl$_5$ solution |                |          |          |          |
| SEM, XPS, XRD, Electrical     | BaTiO$_3$      |                  | 2.5 mol% | 0.4 mol% | 3.0 mol% |
| Characterization              | 135.49 g       | 44.03 g TiCl$_4$ | 31.22 g  | 0.44 g   | 6.20 g   |
|                               | BaCl$_2$·2H$_2$O |                  |          |          |          |
|                               | 2.5 mol%       |                  |          |          |          |
|                               | NbCl$_5$ solution |            |          |          |          |
| SEM, XPS, XRD, Electrical     | SrTiO$_3$      |                  | 2.5 mol% | 0.4 mol% | 3.0 mol% |
| Characterization              | 187.71 g       | 55.89 g TiCl$_4$ | 39.63 g  | 0.56 g   | 7.87 g   |
|                               | SrCl$_2$·6H$_2$O |                  |          |          |          |
|                               | 2.5 mol%       |                  |          |          |          |
|                               | NbCl$_5$ solution |          |          |          |          |

Abbreviations: SEM, scanning electron microscope; TEM, transmission electron microscope; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction.
Powder XRD measurements were performed on a STOE Stadi P Powder Diffractometer System processed with monochromatic Cu Kα radiation (wavelength 154.056 pm). Patterns were analyzed employing GSAS-II software and ICDD database.

To analyze the electric behavior of the material, the powder is mixed with a silicone resin (Wacker, Elastosil 601 A/B, two-component room-temperature vulcanizable material [RTV-2]). The filler content was defined as 25 wt%, which was found to be the limit for the percolative threshold. This was tested in a series of upfront experiments employing samples with different filler contents where the conductivity of the compound was measured.

The mixtures of powder and resin are homogenized with a vacuum Speed Mixer (DAC 400.2 VAC-P, Hauschild Engineering) to ensure that the samples are void-free. A film of around 500 µm is coated on top of a glass plate with a blade coater and cured at 70°C for 30 minutes. Two sample discs with 6 cm in diameter are cut out and are tested up to 10 kV with a low-noise Heinzinger DC power source. The voltage U is increased in steps of 500 V every 2 minutes, starting from 500 V. The electric current I is measured with a Keithley 6514 System Electrometer averaging the current of each step and the measurement of the two samples. It is well known that polarization effects in dielectric insulation materials can last for hours or sometimes days until an equilibrium current is reached. After 2 minutes, most of the polarization phenomena like atom-, orientation-, and hopping polarization decayed, which was estimated as sufficient, especially for a high throughput of samples and comparison of synthesized materials.

A guarded ring electrode system is used, which is illustrated in Figure 2. The guard ring ensures a homogeneous electric field and defines an exact measurement area. The humidity within the measurement housing is kept below a value of 20% RH using silica drying agents.

The relative permittivity was measured in silicone composite materials with a LCR measuring device (Voltcraft®, LCR-300) at a frequency of 100 Hz.

### RESULTS AND DISCUSSION

#### 4.1 Structural characterization of the microparticles

Figure 3 shows cross-section TEM images of Al₂O₃ flakes with a precipitated functional layer of SrTiO₃ doped with Nb (2.0 mol%)—representative for all other doped samples investigated in this study—before (a) and after calcination at 1050°C in air for 2 hours (b). To reduce complexity, a sample only doped with niobium was chosen for this investigation.

The calcination forces the conversion of loosely precipitated material into individual crystals with a thickness of about 20-40 nm.

To investigate the oxidation states of the doping elements, BTO and STO samples doped with Nb (2.5 mol%), Mn (0.4 mol%), and Ce (3 mol%) are analyzed via XPS. Figure 4.
shows in-depth X-ray photoelectron spectra of the doping elements Nb, Mn, and Ce as well as O of the BTO sample calcined in oxidizing and in reducing atmosphere (dashed line). The resulting fit of the deconvolution is summarized in Table 2. The peak at a binding energy of 209.9 eV is related to an oxidation state of 5+ for niobium as it was anticipated. The signal of the manganese measurement is indicated around 641 eV. However, it is too weak, so no evaluation is possible. Cerium is present in the oxidation state 3+ with an amount of 37% and 4+ with an amount of 63% in oxidizing atmosphere. Calcination under reducing atmosphere leads to a slightly increased amount of Ce3+ and decreased amount of Ce4+ (cf. Table 2). Ce3+ ions are larger than Ce4+ ions and therefore substitute the earth alkaline positions.46 As this introduces additional charges, it is not possible in vast extent. Therefore, the thermodynamic stable CeO2 phase is

*FIGURE 4*  XP spectra of Nb 3d, Mn 2p, Ce 3d, and O 1s for BTO samples calcined in oxidizing and reducing atmosphere (dashed line) [Color figure can be viewed at wileyonlinelibrary.com]

| Sample  | Atmosphere  | Element  | Binding energy [eV] | Area      | Amount [%] |
|---------|-------------|----------|---------------------|-----------|------------|
| BTO     | Air         | Nb5+     | 209.7               | 3600.0    | 100        |
|         |             | Ce3+     | 903.4               | 9094.7    | 37         |
|         |             | Ce4+     | 898.9               | 15134.2   | 63         |
| Forming | gas         | Nb5+     | 209.8               | 4865.9    | 100        |
|         |             | Ce3+     | 904.3               | 12951.8   | 39         |
|         |             | Ce4+     | 900.0               | 20000.0   | 61         |

**Table 2** XPS results of the BTO samples received from deconvolution of the XP spectra

Abbreviation: XPS, X-ray photoelectron spectroscopy.
formed, which can also be detected via XPS in a special peak at 882 eV. This peak is larger under oxidizing atmosphere compared to the small shoulder under reducing conditions.

The XPS spectra of the doping elements Nb, Mn, Ce, and O of the STO sample calcined in oxidizing and in reducing atmosphere (dashed line) are shown in Figure 5. The resulting fit of the deconvolution is summarized in Table 3. Niobium is in oxidation state 5+ independent of the calcination atmosphere. Similar to the BTO sample, the manganese signal is weak but this time it can be evaluated. The oxidation states 2+, 3+, and 4+ are found while Mn⁵⁺ is showing the highest amount in oxidizing atmosphere. Calcination under reducing atmosphere leads to a higher amount of Mn³⁺ and reduced amount of Mn⁴⁺. Again, cerium is present in the oxidation states 3+ and 4+. Compared to the BTO sample, a higher amount of Ce³⁺ independent of the calcination atmosphere can be observed (cf. Table 3). We assume that more Ce⁴⁺ can be incorporated into the BTO lattice because of its tetragonal distortion before the extra CeO₂ phase forms.

In Figure 6, the XRD patterns of air- as well as forming gas-calcined BTO and STO samples are shown. Rietveld refinement revealed that the STO sample shows a secondary phase of rutile TiO₂, independent of the atmosphere. A secondary BaTi₂O₅ phase is formed for BTO calcined in air and a Ba₄Ti₁₂O₂₇ phase under forming gas (cf. Table 4).

The secondary phases indicate a shortfall of earth alkaline metal during precipitation, which can be explained by the high solubility of Sr(OH)₂ and Ba(OH)₂ in water and a resulting incomplete precipitation. The solubility equilibrium is as follows:

\[
\text{Sr}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Sr(OH)}_2 \downarrow \quad (2)
\]

\[
K = \frac{[\text{Sr}^{2+}][\text{OH}^-]^2}{[\text{Sr(OH)}_2]}
\]

\[
K_L = [\text{Sr}^{2+}][\text{OH}^-]^2 = 1.75 \quad (4)
\]
The solubility products were obtained from literature. \( \text{K}_L \) for Ba(OH)\(_2\) is lower than for Sr(OH)\(_2\), which means that Sr(OH)\(_2\) is more soluble than Ba(OH)\(_2\). The filtrate was tested using ICP-MS, which only showed Ba- and Sr ions. This is an additional hint that the hydroxides with a low solubility product were not fully precipitated.

For the samples calcined in air, an extra CeO\(_2\) phase was detected by XRD and XPS. This stable phase segregates because Ce\(^{4+}\) ions cannot be incorporated in any quantity into the titanate phases. With an ionic radius of 101 pm,\(^{48}\) it is most likely that cerium can be incorporated into the BTO and STO lattices, respectively, by substituting earth alkaline positions causing an increase in the overall charge of the crystalline structure. When the concentration of cerium exceeds a certain level, the highly positive charged ions segregate as an extra phase.

The XPS evaluation of the samples calcined under reducing atmosphere showed that the amount of Ce\(^{3+}\) (ionic radius of 115 pm\(^{49}\)) is increasing compared to Ce\(^{4+}\). Therefore, no extra CeO\(_2\) phase is formed.

The doping elements niobium (Nb\(^{5+}\), 61 pm\(^{48}\) and manganese (Mn\(^{4+}\), 65 pm\(^{50}\)) have similar ionic radii as titanium (Ti\(^{4+}\), 68 pm\(^{48}\) and it is well accepted in literature that both substitute titanium places in BTO and STO lattice.\(^{38,39,46}\) Due to the low doping concentrations used for the synthesis, no Nb- or Mn secondary phases are expected and no secondary phases were detected with XRD.

The purpose of the precipitated functional layer around the substrate is to ensure electric current flow between grains. Therefore, the coating of the substrate is one key parameter to look at in an optimized precipitation process. Static light scattering exposed that the resulting particles show minor amount of free precipitate (\(<5\%\)), which emphasizes the use of Al\(_2\)O\(_3\) particles as core because precipitation is promoted at nuclei. Direct comparison of SEM images of the same sample calcined in air and under forming gas (Figure 7) shows that the coating of the samples calcined under forming gas is more homogeneous having less gaps between the grains. Smaller grains result in a more homogeneous distribution and coverage of the Al\(_2\)O\(_3\) flakes. Table 5 summarizes the average size of the resulting grains determined with ImageJ.\(^{42}\)

| Sample     | Atmosphere | Element | Binding energy [eV] | Area     | Amount [%] |
|------------|------------|---------|--------------------|----------|------------|
| STO        | Air        | Nb\(^{5+}\) | 209.8              | 5871.8   | 100        |
|            |            | Mn\(^{3+}\) | 640.4              | 884.4    | 51         |
|            |            | Mn\(^{3+}\) | 642.3              | 382.9    | 22         |
|            |            | Mn\(^{4+}\) | 644.6              | 461.3    | 27         |
|            |            | Ce\(^{3+}\) | 904.2              | 6134.6   | 61         |
|            |            | Ce\(^{4+}\) | 899.2              | 3932.3   | 39         |
| Forming gas|            | Nb\(^{5+}\) | 209.7              | 6535.7   | 100        |
|            |            | Mn\(^{3+}\) | 641.0              | 465.1    | 42         |
|            |            | Mn\(^{3+}\) | 642.0              | 500.0    | 46         |
|            |            | Mn\(^{4+}\) | 645.0              | 136.2    | 12         |
|            |            | Ce\(^{3+}\) | 904.3              | 9592.8   | 74         |
|            |            | Ce\(^{4+}\) | 899.9              | 3306.8   | 26         |

Abbreviation: XPS, X-ray photoelectron spectroscopy.

\[
\text{Ba}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Ba(OH)}_2 \downarrow \tag{5}
\]

\[
K = \frac{[\text{Ba}^{2+}][\text{OH}^-]^2}{[\text{Ba(OH)}_2]} \tag{6}
\]

\[
K_L = [\text{Ba}^{2+}][\text{OH}^-]^2 = 1.29 \tag{7}
\]

The comparison of BTO with STO samples calcined in air show that the grains of STO samples have a regular “cubic” form while the grains of the BTO samples have an irregular shape with a broader size distribution. Different from the STO samples, the XRD patterns of the BTO samples (cf. Figure 6A,B) showed that two different secondary phases are formed depending on the calcination atmosphere, which is reflected in the distinct morphology of grains. Moreover, the BTO sample calcined under oxidizing atmosphere forms another secondary phase with very small grains (20-40 nm). The XRD patterns (cf. inset in Figure 6A) showed very broad reflexes of a CeO\(_2\) phase which indicates—derived from Scherrer’s equation—that these small grains are CeO\(_2\).

There are several reasons for observed differences in grain growth and morphology. Due to the present multi-phase material, an intersection of different phenomena is likely, which is also described in literature. With increasing doping concentration, surface energy anisotropy of crystallographic growth planes is reduced, which leads to a more...
“rounded” shape of crystallites. Compared to oxygen vacancies, the diffusion of cation vacancies in titanates is much slower. Additionally, computer simulations show that the activation energy for diffusion of a titanium vacancy in BTO and STO is much higher than for the Sr-, Ba-, or O vacancies. This implies that cations substituting Ti-lattice positions are the most immobile species. A segregation of dopants which substitute Ti-lattice positions (e.g., Nb and Mn) at grain boundaries due to calcination would lead to hindered migration of grain boundaries and inhibited grain growth.

With decreasing oxygen partial pressure, the concentration of cation vacancies with low mobility is reduced. This leads to an enhanced segregation of dopants at grain boundaries and inhibited grain growth. Additionally, the relative surface energy for some crystallographic orientations is higher for calcination in air compared to a calcination under forming gas.

4.2 Electrical characterization of the composite material

The SEM-BSE image in Figure 8 shows a homogeneous distribution of the ceramic filler within the matrix without settling while cross-linking of the silicone, which is an important aspect to ensure properly functioning composites.

The EJ curves of four in air and under forming gas calcined samples are shown in Figure 9. The materials calcined under forming gas show higher nonlinearity coefficients. The highest nonlinearity coefficient of 7 was achieved for the STO sample calcined under reducing atmosphere.
With increasing ceramic filler, the relative permittivity of the composite material is increasing up to a value of around $\varepsilon_r = 3.1$ at a filler content of 25 wt% (cf. Figure 10).

For the explanation of the nonlinear electric behavior of the composite, it is very likely that two different models are overlapping. The first model is based on varistor theory and is well explained in literature.\textsuperscript{27,30,61} Between two identical grains, a thin layer of the same material with defects and doping elements forms. The Fermi level, $F_E$, in the intermediate layer is different and has defined electrical states $n_t$. To reach a thermodynamic equilibrium, electrons flow until the Gibbs free energy is the same overall. Electrons get trapped by defects and dopants at the grain boundary until the Fermi level is adjusted overall. In equilibrium state, the chemical binding energy for electrons occupying a trap is equal to the electrostatic energy, which is necessary to move an electron from the inside of the grain to the grain boundary. The trapped electrons act as a sheet.
of negative charge with a layer of positive charged donor states on every side of the barrier.

With applied voltage, the band structure changes. Additional electrons can be trapped at the barrier causing a dynamic flow of these charges between the grains and the barrier, which is similar to a thermionic emission process.25

Transferring this model to the present case, the explanation for differences in nonlinearity between reducing and oxidizing atmosphere is as follows:

By doping Sr/BaTiO3 with Nb5+, Mn2+, Mn3+, and Mn4+ charge carriers are introduced which substitute titanium lattice positions. They influence the conductivity within the grains due to their different oxidation numbers.

Calcination at high temperatures in air leads to accumulation of oxygen ions at the grain boundary. Ce3+ and Ce4+ with their large ionic radii accumulate at the grain boundary, too, and stabilize the charges. A potential barrier is formed between two grains (Figure 11), being responsible for nonlinear electric behavior of the material as electric current needs to overcome this barrier. For the function as nonlinear electric material, grain size and grain-grain contact are important factors.

The grains of the samples calcined under forming gas had a smaller or similar size compared to the samples calcined in air. Therefore, grain-grain contact is increased and the number of grain boundaries is higher. However, due to the reducing atmosphere during calcination, the potential barrier between the grains is smaller. The opposite is true for the samples calcined in air. The grains are larger with less grain boundaries and poorer grain-grain contact. Due to calcination in air, oxygen ions can accumulate at grain boundaries and the potential barrier increases.

The lower potential barrier for the samples calcined in reducing atmosphere is compensated by the increasing number of grain boundaries due to smaller grains and vice versa for the samples calcined in oxidizing atmosphere.

In addition to the previously described model, particle-to-particle conduction phenomena need to be considered as well. The composite material can be understood as a series of resistor-capacitor (RC) elements in parallel. The filler particles behave as resistive elements (varistor) and form a capacitive element in alternation with the dielectric matrix (silicone). The composite material is charged when a voltage is applied, which results in a temporary high current flow. During the procedure of different polarization processes, the current decays until steady DC resistance ($R_\infty$) is obtained.

5 | CONCLUSIONS

Doped BaTiO3 and SrTiO3 were precipitated around Al2O3 flake-like particles via a wet-chemical process and calcined in air and under forming gas. TEM cross sections of the particles showed the conversion of loosely precipitated coating to a dense grain structure after calcination. Differences in phase composition were detected via XRD. Due to high solubility of Ba(OH)2 and Sr(OH)2 and a resulting shortfall of earth alkaline metal, secondary phases in addition to BaTiO3 and SrTiO3 are present. The precipitated and calcinated particles on top of the Al2O3 substrate were investigated with SEM, which showed that grain sizes and morphology are influenced by the phase composition and the calcination atmosphere. Due to this complex multiphase material, a differentiation of influencing factors was not possible, but SEM images showed that calcination of the materials under reducing atmosphere leads to a more homogeneous distribution of grains on top of the Al2O3 substrate. Oxidation states of doping elements were evaluated via XPS. Due to the reducing atmosphere, oxidation states are reduced as well.

A SEM-BSE image showed that the ceramic filler is homogeneously distributed within the silicone matrix and emphasizes the use of core-shell approach for the formation of functional microparticles. The determination of the nonlinearity coefficients of filler-silicone composites
showed that samples calcined under forming gas achieve the highest coefficients. A possible working principle is postulated, which combines particle-to-particle and grain-to-grain conduction phenomena. The relative permittivity of the composite material increases with increasing filler content.

The herein described filler can be used for applications in field grading high voltage engineering.

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