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Electrical characterization of grain boundary decorated $SrTiO_3$ ceramics

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Abstract

The intention of the present work was to investigate the influence of the grain size on the electrical properties of Mn decorated $SrTiO_3$ ceramics. To obtain different average grain sizes the samples were prepared by variation of the following sintering conditions: form of the green bodies, heating/cooling ramps, sintering atmosphere, sintering time, and sintering temperature. The grain boundaries of the ceramics were decorated with Mn by diffusion from the ceramics surfaces. Impedance analysis techniques in the scope of time and frequency dependence were used for electrical characterization and accelerated life testing (ALT) measurements were performed to characterize the ageing behaviour.

Keywords: Electrical properties; Grain boundaries; Grain growth; Perovskites

1. Introduction

The increasing miniaturization of electronic circuits requires an equally increasing reduction of the electronic component dimensions. Therefore, the industrially manufactured ceramic multilayer capacitors (CMCs) are also affected by this development.

Solid solutions of $BaTiO_3$ and $BaZrO_3$ (BTZ) have been established as one of the most important compositions for dielectric CMCs. Due to the ferroelectric characteristics in the technically relevant temperature range (e.g. room temperature) $BaTiO_3$ is not well suited for electrical characterizations. In the present work acceptor (Ni) doped $SrTiO_3$ — indicating the same lattice and defect structure but no ferroelectric characteristics — was used as a model material for $BaTiO_3$. The results from the study on $SrTiO_3$ samples can be transferred to $BaTiO_3$.

To receive conclusions about the capacity in the bulk C_b, the capacity in the grain boundaries C_{gb}, the conductivity in the bulk σ_b, the conductivity in the grain boundaries σ_{gb}, and the space charge zone width d_{gb}, the real structure of the grains was idealized by the brick-wall-model (Fig. 1) and measurements in frequency response were performed. Conclusions about the behaviour of the conductivity for shorter times σ_s, the conductivity for longer times σ_l, the leakage current, and the lifetime could be drawn from measurements in the scope of time as well as from accelerated life testing (ALT) measurements.

By comparison to undoped grain boundaries — acting as potential barriers — the barriers became smaller in the case of acceptor decoration (e.g. Mn), because the positive, fixed donors at the grain boundaries are partly neutralized. Thus, the leakage current behaviour, the oxygen vacancy and hole transportation were influenced.

This work aimed at the correlation between the grain size, the decoration and the electrical properties of the material.

2. Sample preparation

The acceptor doped $SrTiO_3$-bulk ceramics were prepared by the standard mixed oxide route. First, the acceptor decoration was precipitated wet chemically by mixing $Ni(NO_3)_2$ and TiO_2. After NO_2, O_2, and H_2O were burned out, $SrCO_3$ was added and the powders were mixed for 4 h (1 h on the planet ball mill, 3 h on the roller bank). Subsequently the powder was calcined for 18 h at 1050°C in air, and then milled again for 3 h on the roller bank, to break up eventual agglomerations. Afterwards the powders were pressed to green bodies in form of an ingot and a pill (Fig. 2).

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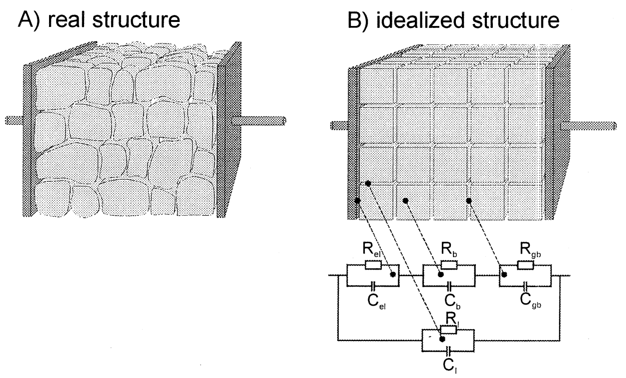

Fig. 1. Brick-wall-model.

For the proximately firing step, the heating/cooling ramps, the sintering atmosphere, the sintering time, and the sintering temperature were varied (to obtain different grain sizes). The influence of each parameter on the grain growth is given in the following figures.

As shown in Fig. 3 the heating/cooling ramps were changed between 120 and 300°C/h. The lower ramp resulted in larger grains and a more homogeneous distribution of grain size, as expected. This result was only observed for a sintering temperature of 1500°C. At 1400°C no differences in grain size were studied.

Fig. 4 represents the influence of the firing atmosphere — air, 2%H_2/Ar, moist (*m*) and dry (*d*) — on the grain growth.

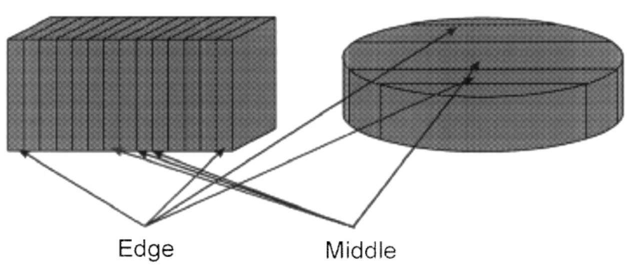

Fig. 2. Green bodies.

A reducing sintering atmosphere was used because of the production of CMCs (Ceramic Multilayer Capacitors), in order to prevent the oxidation of the base metal electrodes. Caused to oxygen losses during the firing process, the $SrTiO_3$ ceramics assumed semi-conducting characteristics.[1] Doping the ceramics with acceptors resulted in a resistance increase, because the acceptors were charge compensated by oxygen vacancies, which were much less mobile than electrons.[2] Under applied voltage oxygen vacancies generated lifetime problems and temperature stress. This problem could be served by an additional reoxidizing step at lower temperatures in comparison to the sintering temperatures or by integration of acceptors (Ni). The determining degradation process of earth alkaline titanates under combined electrical and thermal stress has been described in a well-established model.[3–5]

The samples sintered in air showed the most homogeneous grain sizes distribution but the smallest grain sizes also. In comparison to the samples sintered in dry 2%H_2/Ar atmosphere the samples sintered in moist atmosphere showed larger grains at the edge and nearly the same grain sizes in the middle.

For slower ramps roughly the double grain size was received for samples sintered for 7 h compared to those fired for 5 h (Fig. 5).

The most important influence on the grain growth was given by the sintering temperatures. At a sintering temperature of 1500°C differences in the grain size were observed which amounted a hundredfold of the grain size of the samples sintered at 1400°C. This is shown in Fig. 6.

The samples were cut in slices of 1 mm thickness and afterwards lapped to 700 μm for the decoration. The grain boundary decoration was obtained by diffusion of Mn from the sample surfaces and a subsequent heating step (heating/cooling ramps 100°C/h, maximum temperature 1200°C for 12 h). In the following chapters these samples are denominated as doped samples.

To obtain the desired thickness the samples were lapped again to 500 μm and polished afterwards.

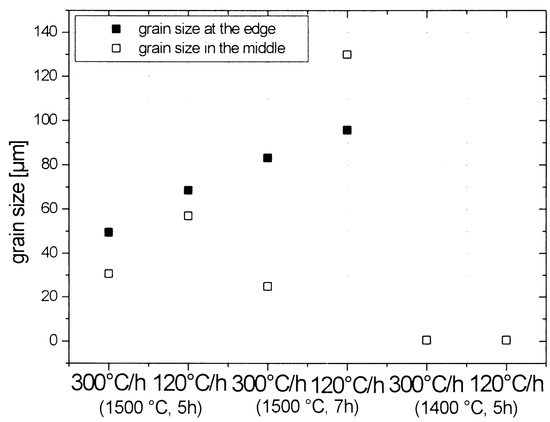

Fig. 3. Grain size as a function of heating/cooling ramps.

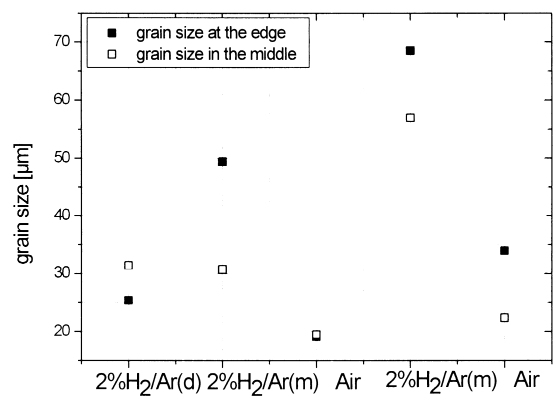

Fig. 4. Grain size as a function of sintering atmospheres.

For the electrical characterization thin NiCr/Ag (100/2000 Å) electrodes were evaporated.

3. Electrical characterization

The dielectric measurements were performed by using impedance analysis techniques in the range of time and frequency response, as well as accelerated life testing techniques. In scope of time the measuring system permitted to measure the small voltages, which emerge on ionic and electronic conductivity in ceramics, by applying a voltage step with a large amplitude (up to 2 kV) on the sample. The measurements led to conclusions about σ_s, σ_l, and the lifetime (Fig. 7).

For the measurements in the frequency response, the frequencies ranged from 5 Hz to 13 MHz at temperatures between room temperature and 500°C (50°C steps). The applied voltage was amounted to 2 kV. By an approximation of the real sample structure to an idealized, the grains and grain boundaries might be described by a parallel connection of *RC*-elements (Fig. 1). The real part of the measurements showed two plateaus, one in the range of lower frequencies and one for the higher frequencies (Fig. 8). From the imaginary part and the following Eq. (1) conclusions about d_{gb} could be drawn.

$$\frac{C_b}{C_{gb}} = \frac{d_{gb}}{d_{gr}} \tag{1}$$

The ALT measurements (Fig. 9) were performed by applying a voltage of 100 V in a temperature range from

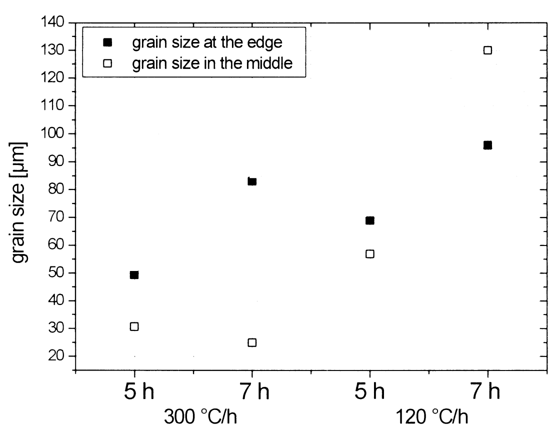

Fig. 5. Grain size as a function of sintering times.

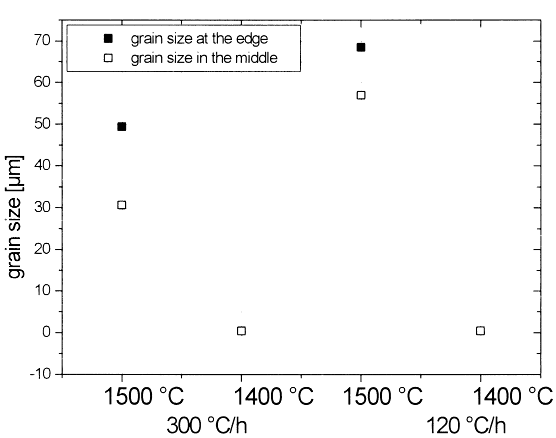

Fig. 6. Grain size as a function of sintering temperature.

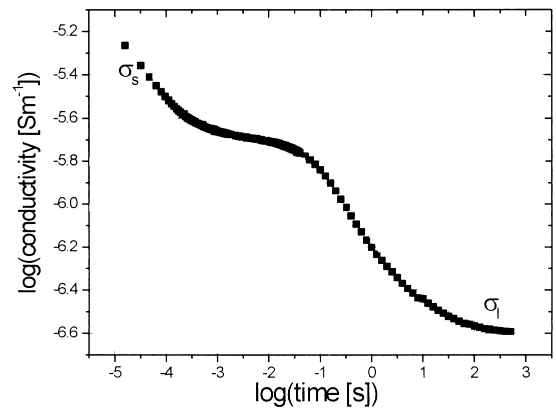

Fig. 7. Conductivity as function of time.

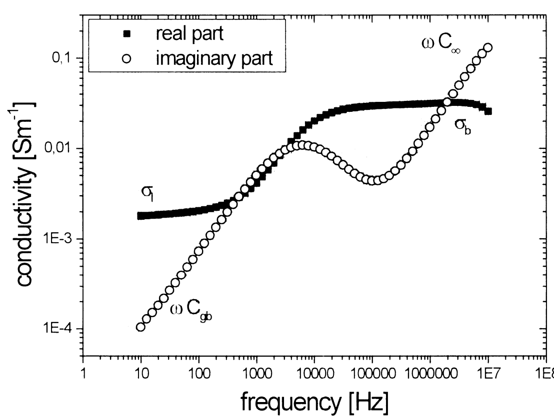

Fig. 8. Conductivity of the real and the imaginary part as a function of the frequency.

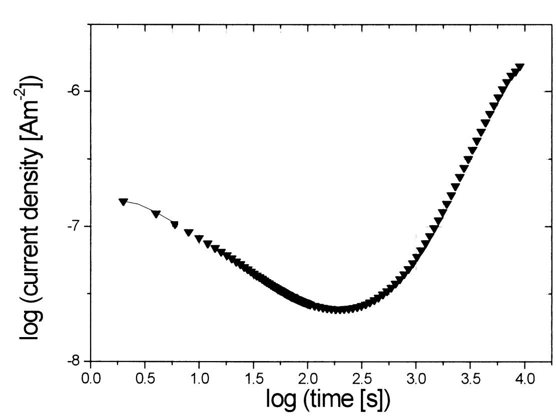

Fig. 9. Current density as a function of the frequency.

25°C up to 225°C (50°C steps). The measuring time was set to 9000 s.

Ageing processes were indicated through a slow increase of the conductivity. The lifetime is the time from the minimum of conductivity to a one decade higher conductivity.

The so-called degradation is of importance, because a change in conductivity by self-heating may lead to a thermal breakthrough.

4. Results

As shown in Fig. 10 σ_b and σ_l depend on the grain size, whereby a larger dependence was observed for σ_b. This is not according to the theory, where σ_b does not depend on the grain size.

Fig. 11 presents the σ_b dependence on the grain size and on the decoration with Mn. As already shown in Fig. 5 the conductivity of bulk increases with increasing grain size, and it increases with Mn decoration also.

Fig. 12 illustrates the imaginary part of conductivity as a function of the frequency. For Mn decoration no influence on C_∞ and C_{gb} was observed.

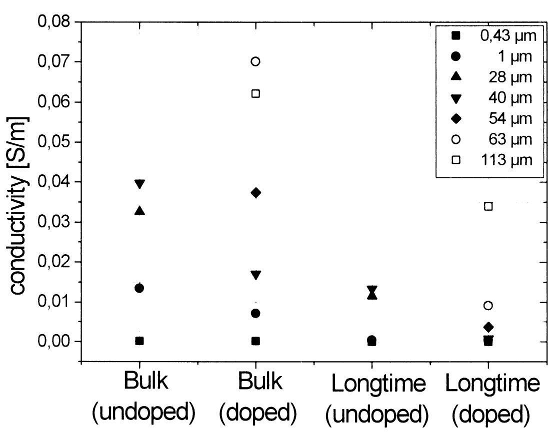

Fig. 10. σ_b And σ_l as a function of grain size and decoration.

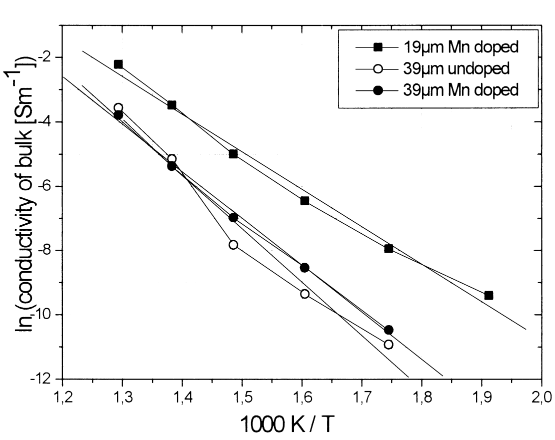

Fig. 11. Arrhenius-plot of σ_b.

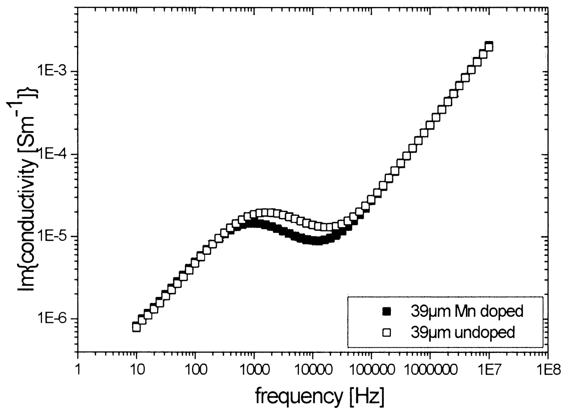

Fig. 12. Influence of Mn-doping on the conductivity as a function of the frequency.

5. Discussion and conclusions

The largest influence on grain growth showed the sintering temperature with different grain sizes in the range of a hundredfold.

The grain growth seems to be dependent on the sintering atmosphere. The maximum is revealed at slightly reductive atmospheres, while it is smaller for strongly reductive and oxidizing atmospheres.

(1) As seen in the figures above some differences to the theory occurred, e.g. the increasing bulk conductivity with increasing grain size (σ_b is independent from grain size); (2) no influence of the Mn decoration on C_{gb} (Mn decreases the grain boundary barrier, therefore the conductivity increases).[6]

For increasing measurement temperature the transition between σ_b and σ_l is reduced. One explanation could be σ_{gb} respectively σ_l needs a higher activation energy, whereby the influence of σ_l could be neglected. A second possibility might be that the activation energy is much higher for σ_b than for σ_{gb} because σ_{tot} shows a W-profile at the grain boundary. This means the potential barrier is thus high, that in the area of the grain boundary the conductivity of electrons is higher than the one of the vacancies.

In the range of time the measurements showed an increasing conductivity for increasing grain sizes and the start of degradation was shifted to shorter times.

Less grain boundaries in the current path and thus the oxygen vacancies have to overcome fewer barriers is one reason for the rising conductivity at increasing grain sizes. It remains to be investigated if the free charge carriers are more mobile in larger grains, or the influence of the electrodes cannot be neglected and the approximation $R_b \ll R_{gb}$ is valid anymore. For increasing grain sizes also C_{gb} increases, hence d_{gb} decreases [Eq. (1)].

The increase of conductivity of bulk (means a lowering of the impedance of the grain boundary ($\sigma_b \propto 1/R_b$)) with increasing grain size does not accord to the theory, because σ_b depends on the mobility of the free charge carriers situated in the grain and their concentration, not on grain size.

The measurements in the frequency response were not ambiguous because the real part of the conductivity increased at high frequencies and did not show the expected plateaus. At high frequencies the measuring instrument reaches its limits so there might be a plateau for much higher frequencies, where all the increasing conductivities of bulk meet.

Due to the fact that the imaginary part showed dispersive behaviour no proposition about d_{gb} can be made. This led to the conclusion that the space charge zone is not exactly distributed all over the sample or that the dopand (Mn) is not uniformly distributed, but cumulated in the gussets or diffused in the bulk.

The decoration with Mn for low frequencies did not show any influence on C_{gb}. This means d_{gb} respectively σ_{gb} stood nearly constant. According to the model of Vollmann/Hagenbeck the conductivity should increase with decoration of Mn.[6,7] A reason that C_{gb} did not increase with decoration, might be the incomplete ionization of the dopand.

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