Journal of the European Ceramic Society 19 (1999) 683–686

PII: S0955-2219(98)00296-9
0955-2219/99/$ - see front matter

Detailed Temperature Dependence of the Space Charge Layer Width at Grain Boundaries in Acceptor-doped $SrTiO_3$-ceramics

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Abstract

The influence of temperature and the donor-type grain boundary (GB) states on the width of the space charge layer d_{GB} *at GBs in* $SrTiO_3$ *ceramics was investigated by comparing numerical simulation results with experimental data. According to recent results for the potential barrier height at the GB, the temperature behaviour of* d_{GB} *can be divided into two different regimes. For lower temperatures,* d_{GB} *is independent of the temperature, for higher temperatures it decreases with rising temperature due to a change in the occupation of the electronic GB donor states. By decorating the GB with suitable dopants, the space charge layer width and its temperature dependence can be influenced. This is due to a change of the effective GB charge.* © *1999 Elsevier Science Limited. All rights reserved*

Keywords: grain boundaries, interfaces, electrical properties, $BaTiO_3$ and titanates, capacitors.

1 Introduction

Acceptor-doped $SrTiO_3$ is regarded as a model material for codoped, net acceptor-doped derivatives of $BaTiO_3$ and $Ba(Ti_{1-x}Zr_x)O_3$ (abbreviated BTZ). This is reasonable due to the similar defect and crystal structure of these perovskite-type materials. $BaTiO_3$ and BTZ are used as high-permittivity-dielectrics in ceramic multilayer capacitors (CMC). The electrically active grain boundaries (GB) are responsible for the high insulation resistance of these dielectrics.[1,2] Due to the sustaining trend of miniaturisation and increasing volume capacities, the dielectric and its grain boundaries are subjected to significantly higher field stresses since the operating voltage remains unaltered.[3] Without countermeasures, this leads to a decreasing life-time of the CMCs. This problem was the motivation for a detailed investigation of the electrical properties of GB barriers in dielectric perovskite-type titanates. The aim is to influence the electrical GB properties technologically in a way that they withstand the higher field stress and the life-time of the complete component does not decrease.

In this paper, we discuss simulation results concerning the influence of temperature on the GB barrier height Φ_{GB} and the width of the GB space charge layer d_{GB}. These electrical GB properties and their temperature dependence can be influenced by decorating the GBs with suitable dopants. The consequences and benefits of GB decoration are also discussed.

2 Microstructure and Electrostatic Spatial Profiles at the Grain Boundary

Figure 1 shows a HRTEM picture of the GB microstructure in a Ni-doped $SrTiO_3$-ceramic. Both neighbouring grains are crystallographically coherent up to the GB due to the details of the preparation process.[4,5] The width of the crystallographically disturbed layer between the adjacent grains is smaller than the extension of two $SrTiO_3$ unit cells. At the GBs, no second phases exist due to the sintering conditions. They only can be found at the triple points where they are electrically inactive. In Fig. 1, a simulation axis is sketched perpendicular to the GB interface. Along this simulation axis, numerical calculations of the spatial distribution of the point defect concentrations and the characteristic quantities of the electrostatic situation were performed. Details of the modelling, the numerical procedure, and the simulation results concerning the spatial GB profiles are described elsewhere.[6–8] Figure 2 illustrates the spatial GB

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profiles along the simulation axis in Fig. 1 of (a) the electrostatic potential Φ and (b) the space charge density ρ. The calculations were performed for a GB in a 0·2 at% Ni-doped $SrTiO_3$-ceramic at a temperature of 523 K. The electrical activity and the potential barrier of the GB region are caused by positively charged donor type states at the GB.[9] The real physical nature of these GB states in acceptor-doped $SrTiO_3$-ceramics is not completely understood yet. Due to reasons of electroneutrality, the positive charge of the GB states is exactly compensated by a negative space charge on both sides of the GB which is built up

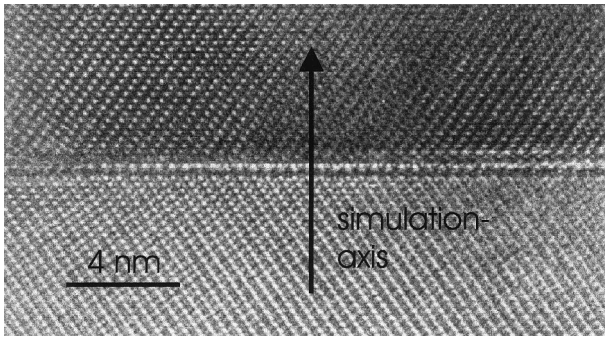

Fig. 1. High resolution transmission electron microscope picture (HRTEM) of a grain boundary in a Ni-doped $SrTiO_3$-ceramic. The electrostatic spatial profiles of Fig. 2 are calculated along the illustrated simulation axis.

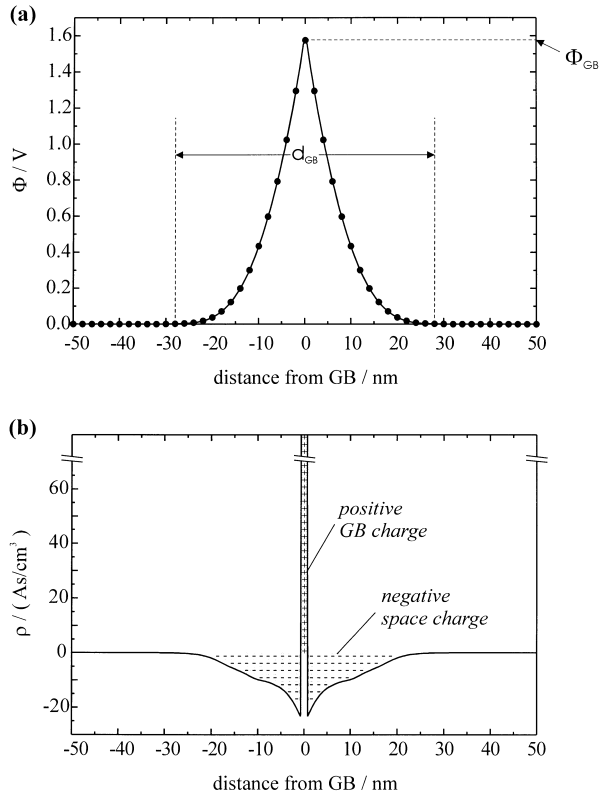

Fig. 2. Simulated spatial GB profiles along an axis perpendicular to the GB interface (see Fig. 1) of (a) the electrostatic potential Φ and (b) the space charge density ρ. The simulations were performed for a GB in a 0·2 at% Ni-doped $SrTiO_3$-ceramic at $T = 523$ K.

mainly by the negatively charged immobile bulk acceptors. Simulation results concerning the temperature dependence of the barrier height Φ_{GB} and the space charge layer width d_{GB} are discussed in the next section.

3 Results and Discussion

The temperature dependence of the GB potential barrier height Φ_{GB} was simulated for 0·2 at% Ni-doped $SrTiO_3$. As an example, Fig. 3 shows the results of such a calculation for a temperature of 523 K. Two different temperature regimes can be distinguished. In regime I, the barrier height increases linearly with increasing temperature. Above a certain transition temperature T_T, Φ_{GB} slightly decreases with increasing temperature. This temperature behaviour can be understood by analysing the following equation for Φ_{GB} which is derived from the simplified Schottky-model for space charge layers but nevertheless describes the real situation at GBs very well:[10]

$$\Phi_{GB} = \frac{Q_{GB}^{\square}}{8 e_0 \varepsilon_0 \varepsilon_r [A']_{eff}} \tag{1}$$

Here, e_0 is the elementary charge, ε_0 is the vacuum permittivity, ε_r is the relative static dielectric constant, $[A']_{eff}$ is the effective concentration of all charged acceptors within the GB space charge region and $Q_{GB}^{\square}$ is the effective GB charge per unit area. Below the temperature GB T_T, all quantities in eqn (1) are independent of the temperature with the exception of ε_r, For $SrTiO_3$, the temperature behaviour of ε_r is described by the Curie–Weißlaw:

$$\varepsilon_r(T) = \frac{C}{T - T_C} \tag{2}$$

C is the Curie constant and T_C is the Curie temperature which equals 28 K for $SrTiO_3$.[11] For the temperature range of the simulation results in Fig. 55, T_C can be neglected and therefore, ε_r is inversely proportional to the temperature leading to the simulated linear increase of the barrier height Φ_{GB} below the transition temperature T_T. Above T_T, the GB charge $Q_{GB}^{\square}$ begins to decrease with rising temperature as illustrated by the simulation result in Fig. 4. This behaviour is due to the decreasing distance between the energy levels of the GB donor states on the one hand and the Fermi level on the other hand which is caused by the strong band bending at the GB. The consequence of this temperature related phenomenon is a significant change in the probability of occupation of

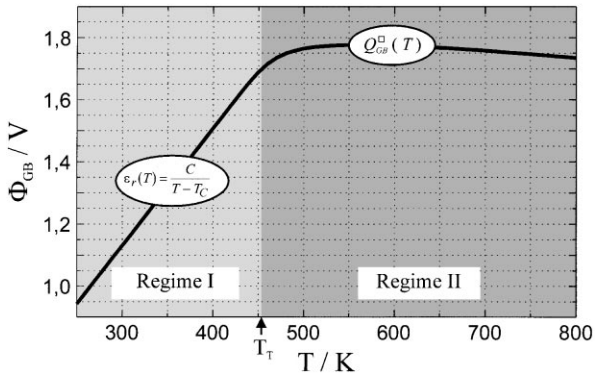

Fig. 3. Simulated temperature dependence of the GB barrier height Φ_{GB} for a 0·2 at% Ni-doped $SrTiO_3$-ceramic. T_T is the transition temperature between linear increase and decrease of Φ_{GB}.

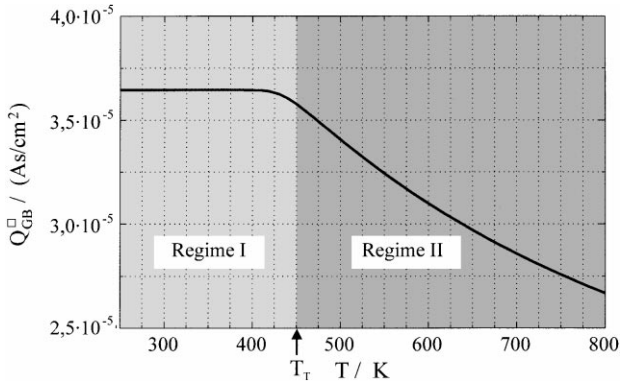

Fig. 4. Simulated temperature dependence of the GB charge density $Q^{\square}_{GB}$ for a 0·2 at% Ni-doped $SrTiO_3$-ceramic. At T_T, the temperature behaviour of Q_{GB} changes.

the GB states leading to the observed decrease of $Q^{\square}_{GB}$.

The temperature dependence of the space charge layer width d_{GB} at the GB also can be interpreted using an equation derived from the Schottky model:[3,12]

$$d_{GB} = \frac{(Q^{\square}_{GB})^2}{e_0[A']_{eff}} \tag{3}$$

Figure 5(a) shows the simulated temperature dependence of d_{GB} for a 0·2 at% Ni-doped $SrTiO)_3$-ceramic and for different interface densities of GB donors D_{GB}. According to eqn (3), d_{GB} and $Q^{\square}_{GB}$ qualitatively show the same temperature dependence due to the temperature independence of $[A']_{eff}$. Below the transition temperature T_T, d_{GB} is constant. Above T_T, it decreases linearly.

The value of the transition temperature T_T can be influenced by decorating the GBs with suitable dopants. Increasing the density $D^{\square}_{GB}$ of donors by GB decoration with La or Nb leads to a decrease of T_T. The artificially added GB donors enhance the effective amount of positive GB charge and the height of the potential barrier. Therefore, the GB potential barrier already gets relatively large at lower temperatures. This effect increases the probability of occupation of the GB donor states

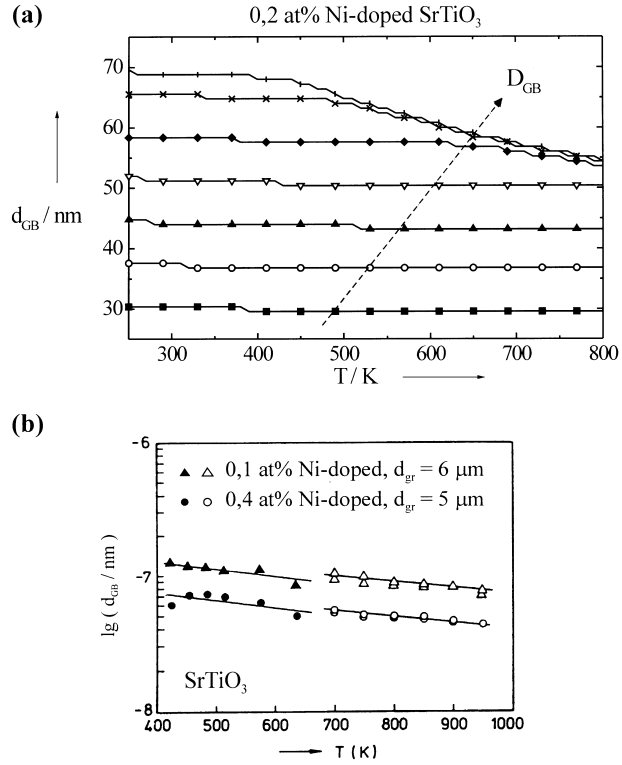

Fig. 5. (a) Simulated and (b) experimentally determined[3] temperature dependence of the GB space charge layer width d_{GB} for Ni-doped $SrTiO_3$-ceramics. D_{GB} is the number of GB donors per unit area.

already at lower temperatures leading to the observed decrease of d_{GB} at relatively low temperatures compared to the case without GB donor decoration. Decorating the GBs with acceptors such as Mn leads to the inverse effect. The negatively charged acceptors partially compensate the positively charged native GB donors. This compensation effect decreases both the effective GB charge and the barrier height and stabilises the temperature dependence of the space charge layer width at the GB.

Figure 5(b) shows the experimentally determined temperature dependence of d_{GB} for Ni-doped $SrTiO_3$-ceramics.[3] The results show a continuous decrease of d_{GB} over the whole temperature range. Obviously, the effective amount of positively charged GB states is so large that the impedance–spectroscopical experiments were carried out above the transition temperature T_T of the investigated probes.

4 Conclusion

The temperature behaviour of the GB potential barrier height Φ_{GB} and the space charge layer width d_{GB} in acceptor-doped $SrTiO_3$-ceramics was investigated using a numerical simulation technique. Acceptor-doped $SrTiO_3$ is regarded as a model material for perovskite ceramics which are used as high-permittivity dielectrics in multilayer

capacitors. Based on the results presented in this paper, we conclude the following:

1. The temperature dependence of the potential barrier height, Φ_{GB}, at GBs in acceptor-doped $SrTiO_3$-ceramics can be divided into two different regimes. Below a certain transition temperature T_T, Φ_{GB} increases linearly with increasing temperature. Above T_T, it shows a slight linear decrease. The explanation for this temperature behaviour of Φ_{GB} is given by the temperature dependence of the relative static dielectric constant ε_r and the effective GB charge per unit area $Q_{GB}^{\square}$.
2. The temperature behaviour of the GB space charge layer width, d_{GB}, can also be divided into two different regimes which are separated by the same transition temperature, T_T, as for the barrier height. Below T_T, d_{GB} is temperature independent. Above T_T, d_{GB} decreases linearly. This temperature dependence of d_{GB} is caused by the temperature characteristic of the effective GB charge per unit area $Q_{GB}^{\square}$.
3. The temperature dependence of both the GB barrier height and the space charge layer widh can be influenced by decorating the GBs with suitable dopants.

Acknowledgements

The authors would like to thank M. Vollmann and U. Weber for the measurements of impedance spectra.

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