

# Characterization of electrical properties of n-conducting barium titanate as a function of dc-bias and ac-voltage amplitude by application of impedance spectroscopy

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**Abstract** The electrical properties of bulk and grain boundaries of donor-doped barium titanate ceramics have been characterized as a function of temperature (50–350 °C) and voltage load (up to 140 V) by application of impedance spectroscopy. Both the grain boundary resistivities and the steepness of the  $R$ - $T$  characteristics are diminished significantly with increasing voltage load. While the grain boundary resistances are strongly affected by the applied electric field, the grain boundary capacitance is almost independent of the dc-bias. The non-linearity of the resistivity of n-conducting BaTiO<sub>3</sub> has been investigated in detail by impedance spectroscopy as a function of dc-bias and a small ac-voltage signal as well as impedance measurements with high ac-voltage amplitudes (zero bias). The non-linear current response to high ac-voltage amplitudes at low frequencies (0.01 Hz) has been determined experimentally and analyzed by means of fast Fourier transform (FFT) as well as Lissajous analyses. Moreover, a finite element model (FEM) has been developed for the simulation of the ac-current response. The FEM calculations are in close agreement with the experimentally determined data for the variation of the grain boundary resistance with ac-voltage amplitude.

**Keywords** Donor-doped BaTiO<sub>3</sub> ceramics · Non-linear grain boundary resistivity · Impedance spectroscopy · Voltage load

## Introduction

Doped barium titanate ceramics represent an important electroceramic materials class with wide-spread technological applications, such as positive temperature coefficient of resistivity (PTCR) thermistors. It is well-known that the electrical properties of n-conducting BaTiO<sub>3</sub> are mainly governed by grain boundaries [1–4]. Therefore, donor-doped BaTiO<sub>3</sub> can be regarded as a model system for interfacially controlled electroceramics which is characterized by various interesting peculiarities with respect to its transport properties. (i) The resistivity of grain boundaries in BaTiO<sub>3</sub>-based PTCRs increases rapidly by many orders of magnitude above the paraelectric-ferroelectric phase transition temperature (Curie-point) [2, 3, 5]. This so-called positive temperature coefficient (PTC) effect is mainly caused by double Schottky barriers at the grain boundaries [6, 7]. (ii) At high temperatures, the grain boundaries provide extremely fast diffusion paths for the transport of oxygen, resulting in selective re-oxidation of grain boundary regions during the cooling process after sintering [8–10]. (iii) The resistivity of the bulk of n-conducting BaTiO<sub>3</sub> is almost negligible in comparison to the grain boundaries, if the ceramics is doped with small amounts of donors (e.g., 0.2 mol-% La). At slightly higher dopant concentrations, the bulk resistivities at room temperature increase tremendously, preventing a clear observation of the PTC effect due to the highly insulating behavior of the bulk [11, 12].

Since the electrical properties of the paraelectric phase of n-type BaTiO<sub>3</sub> (at temperatures above the Curie-point) are determined by double Schottky barriers at grain boundary regions, the resistivity depends strongly on the voltage load [13–15]. The detailed study of the electrical properties under high-field conditions is crucial for a better understanding of the PTC effect as well as for the optimization of technologically relevant PTC resistors.

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It is the aim of this contribution to provide a careful experimental investigation of the non-linear electrical properties of donor-doped barium titanate ceramics under voltage load. Impedance spectroscopy is a powerful technique [16–18] for the determination of the bulk and grain boundary resistivities as well as grain boundary capacitances as a function of dc-bias. In addition to measurements as a function of dc-bias, using a small ac-voltage signal (linear response), complementary experiments are carried out by application of high ac-voltage amplitudes (no dc-bias). The non-linearity of the measured current response to high ac-voltage amplitudes is analyzed by means of fast Fourier transform (FFT) and Lissajous analyses.

## Experimental

Commercially available disk-shaped samples of donor-doped n-conducting BaTiO<sub>3</sub> (EPCOS, Deutschlandsberg, Austria) were investigated by means of impedance spectroscopy. The specimens contain 7.5 mol-% Ca (with regard to the cation content) and are co-doped with Y and Mn [19, 20]. The size was 9.98–10.06 mm diameter and 0.508–0.511 mm thickness. The mean grain size was around 4 μm, which was determined by SEM in previous studies [19, 20]. The samples were metallized by a Ag/NiCr-layer and were used as delivered. The specimens were positioned between two gold foils and were held by light spring action in a quartz reactor. The wires in the reactor were made of gold. The inductance of the sample holder was determined by short-circuit measurements and was about 0.60 μH. Heating was realized using a tube furnace controlled by a Eurotherm 2416 temperature control unit. The actual sample temperature was determined by a K-type (Ni/CrNi) thermocouple and recorded by a Labview© routine. A Novocontrol Alpha-A High Resolution Dielectric Impedance Analyzer with a Novocontrol Broadband High Voltage Booster HVB 300 was used to carry out impedance measurements. The frequency range was between 10<sup>-2</sup> and 10<sup>6</sup> Hz, with 48 frequency points for each spectrum. The default effective ac-voltage was set to 1.0 V<sub>rms</sub>. The integration time was set to 5.0 s or 1 period. All measurements were carried out in 2-wire mode.

A resistance vs. temperature curve was measured between 50 and 350 °C with a step size of about 10 °C with a ramp of 1 °C/min and a dc-bias program as follows: 0, 10, 20, 30, 40, and 80 V. Between each dc-bias setpoint, a zero bias measurement was employed to realize thermal equilibration of the sample.

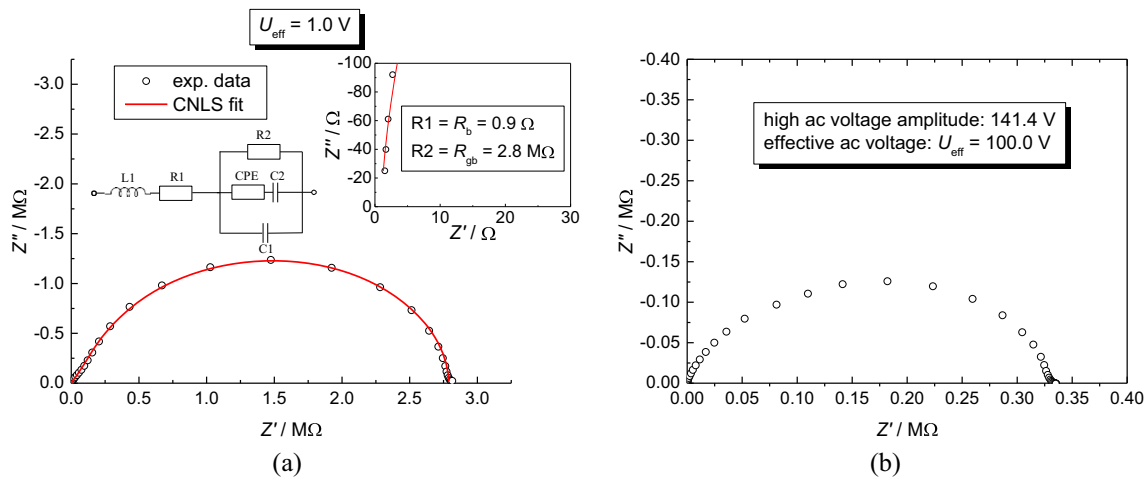
A dc- as well as an ac-variation was carried out at 180, 220, and 300 °C. The dc-bias program was 0, 10, 20, ..., 140 V with two zero bias measurements between each dc-setpoint. The ac-amplitude scan covered a range of 1, 10, 20, 30, ..., 100 V<sub>rms</sub> with two measurements at 1.0 V<sub>rms</sub> between each

ac-setpoint. After several measurements under voltage load, a slight degradation of the metallization could be observed most probably owing to oxidation of the CrNi layer, resulting in enhanced room temperature resistivities due to the evolution of an additional electrode resistance.

Furthermore, the non-linear current response to ac-voltages of high amplitude at low frequencies, where the capacitive displacement currents can be neglected, is measured by means of a high precision multimeter (Keithley 2000). The ac-voltage (sine wave) of high amplitude is applied by a Novocontrol Alpha-A Impedance Analyzer (equipped with a Novocontrol Broadband High Voltage Booster HVB 300) to the n-type BaTiO<sub>3</sub> sample, while the current response at frequencies below 0.1 Hz is recorded as a function of time by a multimeter. Data acquisition is performed by employing a Labview© routine.

## Results and discussion

The evaluation of impedance spectra was performed by using an empirical equivalent circuit developed previously for donor-doped BaTiO<sub>3</sub> ceramics [5], see Fig. 1. The inductance of the empty (short-circuited) sample holder,  $L$ , was determined by separate measurements before the impedance experiments on BaTiO<sub>3</sub> samples were carried out. The bulk resistance,  $R1=R_b$ ; the grain boundary resistance,  $R2=R_{gb}$ ; the CPE-element; and the capacitances  $C1=C_{gb}$  and  $C2$  were determined by a CNLS-fitting procedure of the empirical equivalent circuit to experimental impedance spectra (complex plane plots of  $Z''$  vs.  $Z'$ ). For a more accurate determination of the fitting parameters, the spectroscopic Bode-plots of the real parts of capacitance and resistance were taken into account simultaneously. While  $C1$  can be clearly attributed to the grain boundary capacitance, the origin of  $C2$  is only vaguely known. The quantity  $C2$  might be related to inactive grain boundaries or to the electrodes [5]. Small-angle grain boundaries or Σ3 twin boundaries do not show the PTC effect [1]. Basically, the CPE– $C2$  sub-circuit might also be related to the ionic path associated with the transport of oxygen vacancies along grain boundary regions (ionically blocking electrodes) [18]. It should be mentioned that the bulk concentration of oxygen vacancies in n-conducting BaTiO<sub>3</sub> is negligibly low, and the cation vacancies are certainly frozen-in at temperatures around 300 °C. Typical examples for the complex plane plots are depicted in Fig. 1. Interestingly, a second semicircle was observed during dc-bias and ac-voltage amplitude experiments in the temperature range of about 140–180 °C. This second semicircle could be addressed to self-heating under voltage load and occurs at higher voltages (typically above 80 V). Electrode effects can be ruled out because of the linear increase of the second semicircle with increasing sample thickness. In addition, Ag/NiCr electrodes, usually



**Fig. 1** **a** Complex plane impedance plot ( $Z''$  vs.  $Z'$ ) for n-conducting  $\text{BaTiO}_3$  ceramics under zero bias at  $300^\circ\text{C}$  (effective ac-voltage  $U_{\text{eff}}=1.0$  V). *Inserts* show the equivalent circuit used for data analysis and the magnification of the high frequency part, respectively. **b**  $Z''$  vs.  $Z'$  for

conducting  $\text{BaTiO}_3$  ceramics at  $300^\circ\text{C}$  and effective ac-voltage  $U_{\text{eff}}=100.0$  V. Only  $R_{\text{gb}}=0.33$  M $\Omega$  was determined from these data. (Sample dimensions 1.0 cm diameter; 0.05 cm thickness)

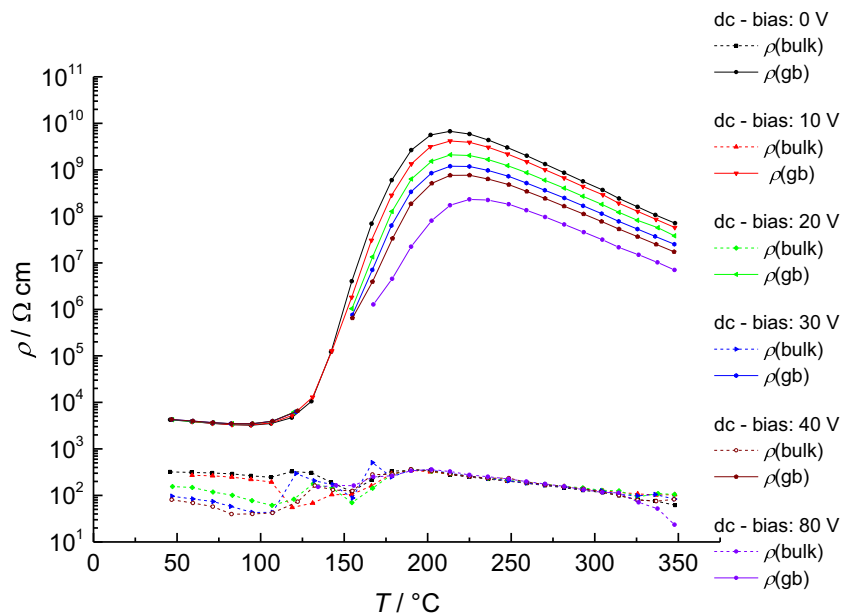
used for n-type  $\text{BaTiO}_3$  ceramics, are ohmic contacts with negligible electrode resistance [21]. Moreover, it should be mentioned that the second semicircular arc was found to be almost independent of the applied field. Since only the first semicircle can be unambiguously attributed to the grain boundaries, the second arc was disregarded for the data fitting procedure.

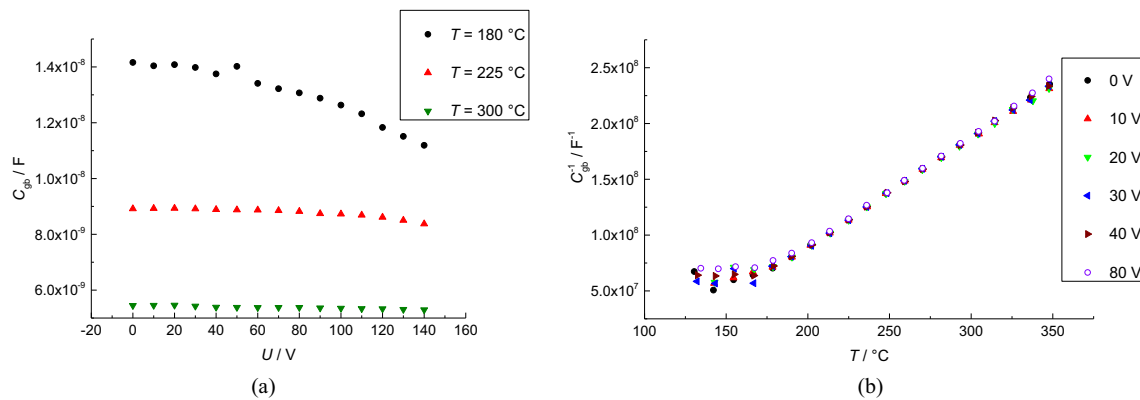
The temperature characteristics of both the bulk and grain boundary resistivities are depicted as a function of dc-bias in Fig. 2. While the bulk resistivity is almost independent of temperature and dc-bias, the grain boundary resistivity shows the PTC effect, i.e., a steep increase by many orders of magnitude above the Curie-point (approximately  $120^\circ\text{C}$ ). Moreover, the grain boundary resistivities decrease remarkably with increasing dc-bias, resulting in  $R$ – $T$  characteristics with diminished

steepness under voltage load in the temperature range from  $120$  to  $200^\circ\text{C}$ . It is worthwhile mentioning that in the negative temperature coefficient (NTC) regime, at temperatures above approximately  $200^\circ\text{C}$ , the slope  $d \ln R/d T$  is almost unaffected by the dc-bias, see Fig. 2.

The variation of the grain boundary capacitance,  $C_{\text{gb}}$ , with dc-bias is plotted for three temperatures in Fig. 3a. Whereas at  $180^\circ\text{C}$ , the capacitance decreases somewhat with increasing voltage load above 40 V; the grain boundary capacitance is almost independent of dc-voltage at  $225$  and  $300^\circ\text{C}$ . The Curie-Weiss plot for the grain boundary capacitances is shown in Fig. 3b. It can be deduced that the temperature dependence of  $C_{\text{gb}}$  is much more pronounced than its variation with voltage load.

**Fig. 2** Grain boundary,  $\rho$  (gb), and bulk resistivity,  $\rho$  (bulk), of n-conducting  $\text{BaTiO}_3$  vs. temperature at various dc-bias values





**Fig. 3** **a** Grain boundary capacitance of n-type BaTiO<sub>3</sub> vs. voltage at three temperatures. **b** Curie-Weiss-plot of grain boundary capacitance for various dc-bias values. (Sample dimensions 1.0 cm diameter; 0.05 cm thickness)

The grain boundary resistances are plotted as a function of voltage load in Fig. 4 for three temperatures. Basically, the grain boundary resistances (solid circles) extracted from impedance spectra with small ac-amplitude (dc-bias variation and effective ac-voltage of 1.0 V) are consistent with the slope  $dU/dI$  of the current–voltage curve. The discrepancy between results from the dc-bias variation and the slope of the  $I$ – $V$  curve at 180 °C and a dc-voltage above 80 V might be attributed to self-heating of the n-type BaTiO<sub>3</sub> samples during the impedance measurements under voltage load (Fig. 4a). The resistance data (open circles) obtained from the ac-voltage amplitude variation are significantly higher than the dc-bias data. In this case, the grain boundary resistances are roughly consistent with the ratio  $U/I$  of the non-linear current–voltage curve. As the impedance spectra at high ac-voltage amplitudes are generated from the first harmonic base wave of the non-linear current response, the resistance values of the ac-amplitude variation are exactly given by the ratio  $U/I$  of the harmonic base wave at low frequencies.

The non-linear current response at a frequency of 0.01 Hz and an effective ac-voltage of 100 V is depicted in Fig. 5a. At low frequencies, no phase shift between voltage and current signals is expected owing to a vanishing displacement current. Hence, the non-linear behavior of the ac-current at 0.01 Hz is exclusively determined by the non-linear resistance of n-conducting BaTiO<sub>3</sub> ceramics (interfacially controlled electroceramics). It is worth mentioning that the displacement current (relevant at high frequencies) is anticipated to be linear, as the capacitance is almost independent of the voltage load (see Fig. 3a). Furthermore, the non-linearity of the measured ac-current signal at 0.01 Hz is confirmed by the fast Fourier transform (FFT), see Fig. 5b. Apart from the harmonic base wave at 0.01 Hz, additional peaks due to higher harmonics are visible at 0.03, 0.05, and 0.07 Hz, respectively.

Moreover, a finite element model has been developed for calculations of the current response to ac-voltage signals (sine waves) with high amplitude. It should be noted that finite element model (FEM) simulations of impedance spectra for

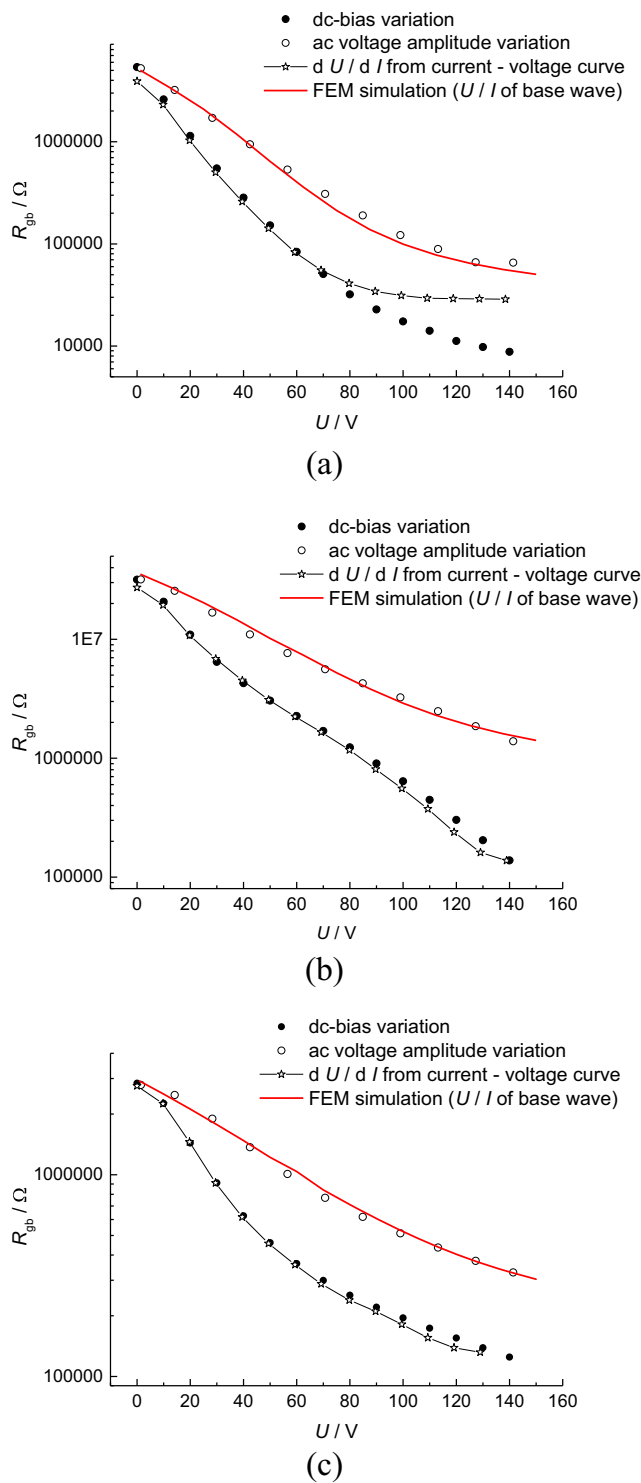
small ac-amplitudes (linear response) can be found in, e.g., Refs. [22, 23]. Basically, the continuity equation for the current density

$$\text{div } j = 0 \quad (1)$$

is solved by application of the finite element method (COMSOL Multiphysics© 5.0). The ac-current density can be written as

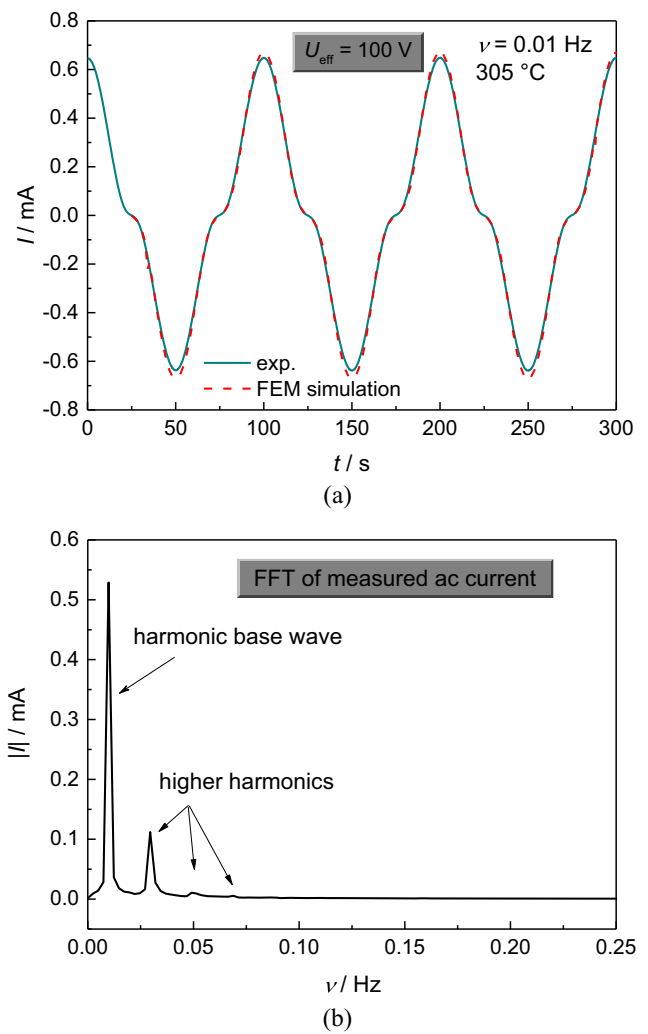
$$j = - \left( \sigma + \varepsilon \varepsilon_0 \frac{\partial}{\partial t} \right) \text{grad } \phi, \quad (2)$$

where  $\sigma$  and  $\varepsilon$  denote the electronic dc-conductivity and relative permittivity of n-type BaTiO<sub>3</sub>, respectively, and the symbols  $\varepsilon_0$  and  $\phi$  refer to the permittivity of vacuum and the electric potential. It should be noted that both  $\sigma$  and  $\varepsilon$  are independent of frequency regarding the present finite element model. For the sake of simplicity, 2D-FEM simulations are performed on a square with a side length of 1 cm, assuming ohmic contacts (i.e., electrode resistances are disregarded). A sine wave voltage is applied to one side (surface) of the square, while the opposite side (surface) is set to ground. The remaining sides may be electrically insulating. The mesh consists of more than 9000 triangular elements with a maximum element size of 0.067 cm. An exponential decay function is fitted to the experimental results for the grain boundary resistivity as a function of dc-bias (solid circles in Fig. 4). This fit function is implemented into the FEM software (COMSOL Multiphysics© 5.0) in order to take account of the non-linear (voltage-dependent) conductivity of n-type BaTiO<sub>3</sub>. As the capacitance is almost independent of the voltage load (Fig. 3a), a constant relative permittivity has been employed for the simulations. Figure 5a reveals that the simulated non-linear current response for an effective ac-voltage of 100 V and a frequency of 0.01 Hz is in close agreement with the measured current. In addition, the ratio of the peak voltage and the current amplitude of the harmonic base wave ( $U/I$ ), extracted from the FEM simulations, coincide remarkably well with experimental results for the

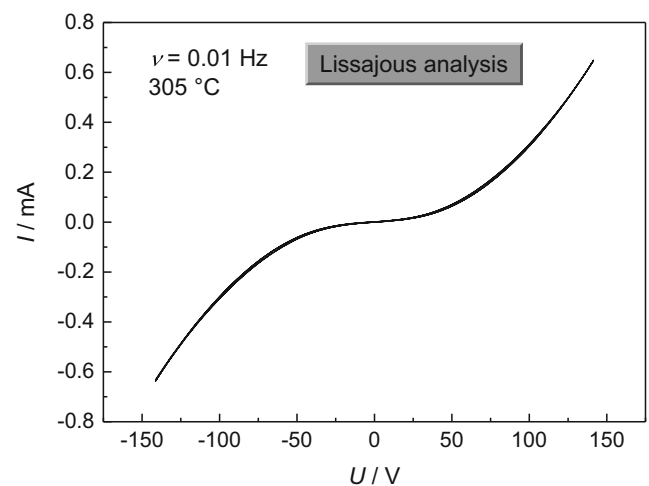


**Fig. 4** Grain boundary resistance of n-conducting BaTiO<sub>3</sub> plotted vs. voltage load. Data are based on dc-bias variation (small effective ac-voltage, 1.0 Vrms) as well as ac-voltage amplitude variation. Numerical differentiation of the experimental  $I-V$  curve and FEM simulations ( $U/I$  of harmonic base wave) are likewise shown. **a** 180 °C, **b** 225 °C, and **c** 300 °C. (Sample dimensions 1.0 cm diameter; 0.05 cm thickness)

grain boundary resistance obtained from the ac-voltage amplitude variation, see Fig. 4.

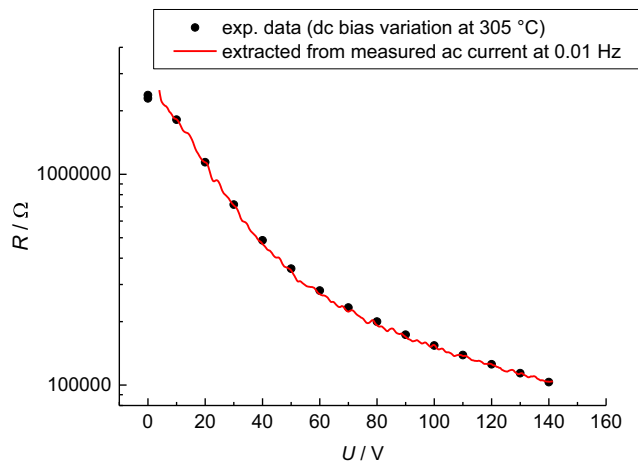


**Fig. 5** **a** Measured as well as simulated (FEM) current response at a frequency of 0.01 Hz (effective ac-voltage 100 V) for n-type barium titanate at  $T=305 \text{ }^\circ\text{C}$  (sample dimensions 1.0 cm diameter; 0.05 cm thickness). **b** FFT of measured current (effective ac-voltage 100 V; 0.01 Hz)



**Fig. 6** Lissajous analysis of measured ac-current at 0.01 Hz (Fig. 5a)





**Fig. 7** Grain boundary resistance of n-conducting barium titanate vs. dc-bias at 305 °C (sample dimensions 1.0 cm diameter; 0.05 cm thickness). Comparison between results from impedance spectroscopy (small ac-voltage, 1.0 Vrms) and first derivative of current–voltage curve extracted from Fig. 6 (Lissajous plot)

A Lissajous analysis [16, 17] of the measured non-linear current response (Fig. 5a) to a sine wave voltage signal with amplitude of 141.4 V at 0.01 Hz is shown in Fig. 6. Basically, the lines depicted in Fig. 6 are consistent with the current–voltage curve of n-type BaTiO<sub>3</sub>, as the phase shift between voltage and current signals is negligible at this frequency. From Fig. 7, one can deduce that the first derivative of the  $I$ – $V$  curve, obtained from Fig. 6, is in perfect coincidence with resistance values based on impedance spectroscopy (dc-bias variation, small ac-voltage).

## Conclusions

The electrical properties of n-conducting barium titanate ceramics have been investigated as a function of temperature and voltage load by application of impedance spectroscopy. Basically, the grain boundary resistivity decreases remarkably under voltage load owing to the non-linear nature of the electrical properties of Schottky barriers at the grain boundaries. Additionally, the steepness of the temperature characteristics of the grain boundary resistivity decreases significantly with increasing dc-bias. Apart from the determination of the bulk and grain boundary resistances and the grain boundary capacitance as a function of dc-bias using a small ac-voltage signal (linear response), the non-linear grain boundary resistivity has been investigated by impedance measurements with high ac-voltage amplitude. Whereas the results from the dc-bias variation (small ac-voltage) correspond to the slope of the  $I$ – $V$  curve, the resistivities obtained from measurements at high

ac-voltage amplitude (no dc-bias) are given by the ratio of the peak voltage and current amplitude of the harmonic base wave which has been confirmed by appropriate FEM simulations. Hence, a significant inconsistency between resistance values, obtained from impedance spectroscopy at a given dc-bias (small effective ac-voltage), and data, extracted from impedance measurements at the same ac-voltage amplitude (no dc-bias), would indicate a non-linear behavior of the electrical properties of the sample. Moreover, the non-linearity of the grain boundary resistance of n-type BaTiO<sub>3</sub> has been studied by means of fast Fourier transform (FFT) and Lissajous analyses.

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