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Conductivity relaxation experiments on donor doped barium titanate ceramics: Effect of microstructure

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ABSTRACT

The re-equilibration kinetics of n-conducting $BaTiO_3$ ceramics upon a sudden change of the oxygen partial pressure of the surrounding gas phase has been investigated by application of conductivity relaxation experiments at 900 °C using the van der Pauw method. The relaxation curves show two distinct equilibration processes. The first (fast) relaxation refers to diffusion of oxygen most probably via oxygen vacancies along the core regions of grain boundaries. The second (sluggish) relaxation process is related to slow diffusion of cation vacancies from the grain boundaries into the bulk. Even after 1000 h, disk-shaped samples with an average grain size of 4 μm and thicknesses between 0.5 and 1.0 mm are not fully equilibrated with the gas phase. A modified Schottky barrier model, taking account of diffusion profiles of cation vacancies at the grain boundaries, enables a phenomenological interpretation of the conductivity relaxation curves. In addition, the defect chemistry of core regions of grain boundaries in n-type $BaTiO_3$ ceramics has been studied by conductivity measurements as a function of oxygen partial pressure [$0.5 > p(O_2)/\mathrm{bar} > 0.001$].

1. Introduction

The electrical properties of functional electroceramic materials, such as $BaTiO_3$ — based PTC (positive temperature coefficient) resistors, are strongly affected by re-oxidation processes during annealing at certain well-defined temperatures and oxygen partial pressures as well as the cooling period after sintering at high temperatures. A detailed knowledge of oxygen exchange reactions at the surface and transport of oxygen in the bulk as well as grain boundaries is inevitable for the development of novel materials and the optimization of preparation and processing procedures [1]. Fast diffusion of oxygen along grain boundaries plays a key role for the re-oxidation kinetics of interfacially controlled materials, such as n-conducting $BaTiO_3$ — based PTC thermistors [2–9]. It is worth mentioning that the transport properties of grain boundaries are affected by space charge regions adjacent to the grain boundary core as well as diffusion along the core region which might differ from bulk regions with regard to oxygen non-stoichiometry and defect chemistry [10–12].

Conductivity relaxation experiments are a powerful technique for the investigation of diffusion processes in electroceramics [13–17]. Usually, the oxygen partial pressure of the gas phase is altered instantaneously and the response of the mixed conducting ceramic sample owing to oxygen exchange between the ceramics and the surrounding atmosphere (diffusion source or sink) is determined by means of conductivity measurements as a function of time. A proper analysis of relaxation curves of the electrical conductivity yields relevant kinetic parameters, such as the chemical surface exchange coefficient and the chemical diffusion coefficient of bulk as well as grain boundaries, necessary for a phenomenological description of oxygen exchange processes including re-oxidation kinetics.

It is the aim of this contribution to investigate chemical diffusion processes in n-conducting $BaTiO_3$ ceramics by application of dc conductivity relaxation experiments at 900 °C, employing the four-point van der Pauw method [15,18]. The re-equilibration kinetics is determined by extremely fast diffusion of oxygen along the grain boundaries and slow transport processes of cation vacancies from the grain boundaries into the bulk. The conductivity relaxation curves are interpreted in terms of a modified Schottky barrier model developed recently [8,19]. Moreover, the determination of the electronic conductivity as a function of oxygen partial pressure allows the investigation of the defect chemistry and transport properties of core regions of grain boundaries in PTC resistors.

2. Experimental

Disk-shaped samples of donor (0.5 mol.% Y) and acceptor (0.1 mol.% Mn) co-doped n-conducting barium titanate ceramics, $(Ba_{0.85}Ca_{0.15})TiO_3$, were provided by EPCOS (Deutschlandsberg, Austria), see also Refs. [17,20,21]. The thickness of the specimens ranged from 0.5 to 1.0 mm and the diameter was 10.0 mm. The density of the sintered disk-shaped samples was (5.479 ± 0.033) g cm^{-3} corresponding to 95% relative density. The microstructure was investigated by scanning microscopy (SEM, Stereoscan 250

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MK3, Cambridge Instruments) on polished and chemically etched samples (0.5% HF/5% HCl). The average grain size, extracted from SEM micrographs, was (3.7 ± 1.8) μm (based on four determinations employing the line intercept method). All uncertainties refer to 2σ (95% confidence interval).

The van der Pauw method was used for the conductivity relaxation experiments. Four peripheral point-like contacts were fabricated on the top face of the specimen by Pt — paste which was burned-in at 1000 °C for two hours. A constant direct current (typically 100 μA) was fed through two neighboring contacts by means of a high precision current source (Keithley 2400), while the voltage was recorded between the opposite voltage probes by application of a digital multimeter (Keithley 2000) containing a scanner card necessary for the van der Pauw technique. The conductivity measurements were carried out in a tube furnace, where the temperature was kept constant at 900 °C by means of a Eurotherm 2416 controller. The temperature close to the sample was monitored by a type S (Pt/Pt–Rh) thermocouple. The oxygen partial pressure was varied between 0.001 and 0.5 bar by appropriate gas mixtures of oxygen (99.995%), 1% — O_2/Ar, and argon (99.999%), employing mass flow controllers (Tylan 2900, Mykrolis). The conductivity relaxation experiments were performed by a step-wise alteration of the oxygen partial pressure of the carrier gas and the response of the ceramic sample was recorded by means of van der Pauw conductivity measurements as a function of time, using a LabView© routine for data acquisition. It is worthwhile mentioning that the four-point van der Pauw measurements yield electronic conductivities although the Pt-electrodes are not necessarily ion-blocking at fairly high oxygen partial pressures (10^{-3} — 0.50 bar), since the transport number of electrons in n-type $BaTiO_3$ is almost unity ($t_e \approx 1$) due to much higher mobilities of electronic charge carriers.

3. Results and discussion

The variation of the electronic conductivity of n-type $BaTiO_3$ ceramics with time due to various oxygen partial pressure changes at 900 °C is depicted in Fig. 1. In addition, the long-term behavior of the electronic conductivity (relaxation curve) over a time period of 1000 h after an oxidation step from $p(O_2) = 0.10$ bar to $p(O_2) = 0.50$ bar is likewise shown in Fig. 1 (thick gray line). From Fig. 1 one can deduce that the relaxation curve of the electronic conductivity can be described by a fairly fast transport process and a very slow second re-equilibration process, which corresponds to two different time constants (relaxation times). The sluggish second part of the relaxation curve indicates that at 900 °C even after 1000 h equilibrium between n-conducting $BaTiO_3$ and the gas phase has not yet been attained. Basically, the re-equilibration kinetics of n-type $BaTiO_3$ due to an instantaneous change of the oxygen partial pressure of the surrounding atmosphere is determined by extremely fast diffusion of oxygen along the grain boundaries (usually random large-angle grain boundaries with a thickness of the structurally disordered core region of 0.5 nm [22]) and slow rate-limiting transport of cation vacancies from the grain boundaries into the bulk (grains) [13,16,17,23]. Hence, the relaxation curves depicted in Fig. 1 seem to be related to diffusion processes at grain boundary regions in donor doped barium titanate ceramics. The first re-equilibration process can be attributed to extremely fast transport of oxygen along the grain boundaries involving predominantly core regions. The second relaxation process is caused by slow cation vacancy diffusion from the grain boundary into the bulk which will be elucidated in more detail below.

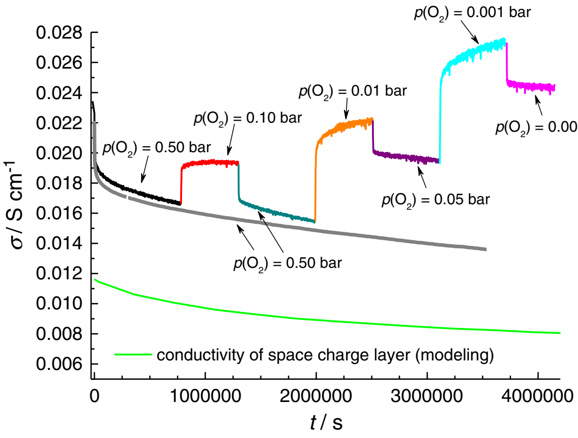

Fig. 1. Relaxation curves of the electronic conductivity of n-type $BaTiO_3$ ceramics at 900 °C for various oxidation and reduction steps. Thick gray line: oxidation step from $p(O_2) = 0.10$ to $p(O_2) = 0.50$ bar; sample dimensions: 1.0 cm diameter and 0.10 cm thickness. Solid lines: various oxygen partial pressure steps; sample dimensions: 1.0 cm diameter and 0.05 cm thickness. Calculated conductivity (green line) of bulk + space charge layer at grain boundaries is based on the modified Schottky barrier model. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The kinetics of the second relaxation process is given by the diffusivity of cation vacancies in the bulk, which has been studied as a function of temperature ($1100 < T/°C < 1250$) previously [17]. Extrapolating these data to lower temperatures yields a chemical diffusion coefficient of $\tilde{D} = 2 \times 10^{-16} \mathrm{cm}^2\ \mathrm{s}^{-1}$ at 900 °C. Applying this kinetic parameter,-diffusion profiles for cation (Ti) vacancies evolving at the grain boundaries owing to oxidation can be calculated numerically by means of finite differences [8]. From these diffusion profiles the characteristic diffusion length (penetration depth) of cation (Ti) vacancies, L_c, can be extracted in accordance with $(c_{V_{Ti}''''} - c_{V_{Ti}'''',0})/(c_{V_{Ti}'''',\infty} - c_{V_{Ti}'''',0}) = \mathrm{erfc}(x/L_c)$, where $c_{V_{Ti}'''',0}$ and $c_{V_{Ti}'''',\infty}$ denote the initial and equilibrium concentrations of cation (Ti) vacancies in the bulk, respectively [8]. The variation of L_c with time is illustrated in Fig. 2. It is worth noting that the initial penetration depth, L_c (at $t = 0$), is caused by the frozen-in diffusion profiles of cation vacancies created during the cooling process after sintering in air at 1350 °C. Usually, the cation vacancy diffusion profiles are frozen-in around 1100 °C (for a typical cooling rate of 4 K/min), see Ref. [8] for more details. Since the samples are initially not fully equilibrated (apart from grain boundary core regions), the initial diffusion profile is taken into account for the numerical calculation of the concentration profiles of cation vacancies at the grain boundaries as a function of time.

At 900 °C the penetration depth of cation vacancies from the grain boundaries into the bulk is only around 0.5 μm after 1000 h because of the slow cation diffusivity at this temperature. However, the increase of the penetration depth of cation vacancies, which are additional acceptor states, results in a significant increase of the depletion zone width of space charge layers at the grain boundaries, leading to the sluggish decrease of the conductivity with time. As the diffusion processes are confined to regions in the vicinity of grain boundaries, the decrease of the electronic conductivity (increase of resistivity) is predominantly

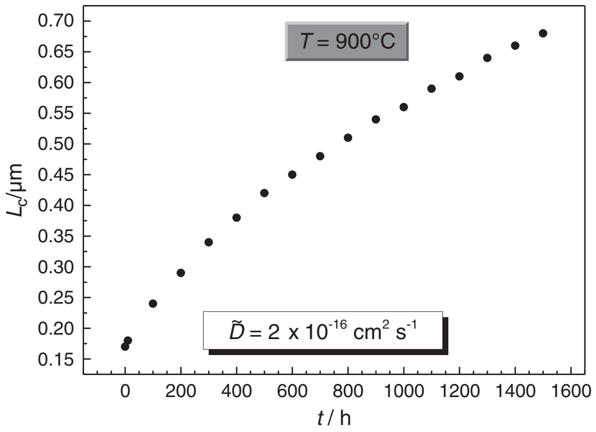

Fig. 2. Calculated penetration depth (characteristic diffusion length) of cation vacancies from grain boundaries into the bulk of n-type $BaTiO_3$ for an oxidation step at 900 °C.

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