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Advances in point defect chemistry: space charge controlled surface reactions

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Abstract

A theoretical point defect model for the transition between two equilibrium states is proposed. Material constants are taken from lanthanum-doped $SrTiO_3$, which serves as a model material for donor-doped perovskites. A finite-differences method is used to compute the time dependent evolution of defect concentrations after an excitation of the system. For the calculation of the particle fluxes of all charged defects, *time variant surface concentrations* of all mobile species are considered via *local defect equilibria*. As the surface concentrations differ significantly from the new equilibrium values, a drastic change of the electrical properties in the near-surface region is expected. The new approach is strongly supported by the resistivity change of the material in an oxidation experiment. A comparison between simulation and experimental data confirms the excellent applicability of the model. © 2001 Published by Elsevier Science Ltd.

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1. Introduction

The investigation of oxygen vacancies as a point defect in perovskites started in the early 60s with tracer and thermogravimetry experiments. It has been demonstrated, that ionic and electronic point defects govern the transport properties of the material. In this publication, we distinguish between intrinsic and extrinsic point defects, which are defined as follows.

Intrinsic defects are vacancies on regular lattice sites of both the oxygen and the cation sublattice. They form at high temperatures, whereas its formation/ removal follows a defect chemical reaction. Donor-doped $SrTiO_3$, that is used in the present investigation, reveals two characteristic defect reactions. Under strong reducing conditions, the dominant process of oxygen vacancy formation[1] (V_O) is given by:

$$O_O^x \Longleftrightarrow \frac{1}{2}O_2(g) + 2e' + V_O^{\bullet\bullet} \tag{1}$$

For the notation of defects, we refer to Kröger and Vink.[2]

For high oxygen activities, a stoichiometry shift in the cation sublattice becomes the predominant process. The formation of strontium vacancies (V_{Sr}) is given by:[1,3–7]

$$\tfrac{1}{2}O_2(g) + 2e' + \mathrm{Sr}_{Sr}^x \Longleftrightarrow V_{Sr}'' + \mathrm{SrO}_{\text{second phase}} \tag{2}$$

The present study will focus on this defect reaction.

Extrinsic defects are substitutions of regular lattice sites by higher or lower valent ions. By trapping and/ or releasing electrons or defect electrons into the crystal, the character of the material significantly changes from insulator to semiconductor. In the case of lanthanum-doping as used in this investigation, the donor is always regarded as singly ionized:

$$\mathrm{La}_{Sr}^x \;\rightarrow\; \mathrm{La}_{Sr}^{\bullet} + e' \tag{3}$$

Considering *local electroneutrality*, all defect concentrations can be calculated as a function of the oxygen partial pressure or the temperature, respectively. Since the electrical properties of donor-doped $SrTiO_3$ are dominated by electrons, the conductivity σ of the material under all experimental conditions is given by

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$$\sigma = e_0 \mu_n n, \tag{4}$$

where e_0 denotes the elementary charge, μ_n the particle mobility and n represents the concentration of electrons. Experimental studies of the conductivity of donor-doped $SrTiO_3$ in the high temperature range confirm a good agreement with the model under various conditions.[1]

Beside the knowledge of homogeneous distributed defect concentrations in thermodynamic equilibrium, the kinetics of transition is the present challenge in understanding effects of technical relevance. Two examples are the resistive sensor characteristics in the high temperature regime[8] and the insulating grain boundaries behavior in the technical temperature range.

The usual way to describe the equilibration of perovskites after a thermodynamic excitation is *to separate* surface defect reactions [Eqs. (1) and (2)] from the propagation of defects into the crystal. It is assumed, that an *instantaneous local thermodynamic equilibrium at the surface fixes the defect concentrations* at temperatures above 1200°C.[4] Hence, *constant* surface concentrations are used as boundary conditions for the diffusion process, which leads to the relaxation of the system. The ambipolar diffusion concept is used to consider the interaction of charged defects by an internal electrical field. For further details, we refer to reference[9] and references given therein.

In contrast to acceptor-doped $SrTiO_3$, an interpretation of the resistivity change after a thermodynamic excitation by the diffusion of defects fails in donor-doped $SrTiO_3$.[4] We regard *time variant surface concentrations* to be responsible for the misfit between theory and experiment. The surface concentrations are shifted by a time variant space charge in the near-surface region. The ambipolar diffusion is regarded as the source for the local deviation from the electroneutrality.

The present work is intended to generalize the common point defect approach, that is limited to electroneutral regions, to local space charges. Surface concentrations calculated under space charge are introduced as time variant boundary conditions for the diffusion process. The relaxation of the system after an external excitation is calculated by a numerical approach.

2. Defect calculation in equilibrium

To calculate the defect concentrations as functions of the temperature T or the oxygen partial pressure pO_2, laws of mass action have to be developed from the defect chemical reactions [Eqs. (1) and (2)]. For the formation of oxygen vacancies, we assume:

$$K_O(T) = n^2 \cdot [V_O^{\bullet\bullet}] \cdot pO_2^{0.5} \tag{5}$$

Analogous, the formation of cation vacancies is given by:

$$K_{Sr}(T) = \frac{[V_{Sr}'']}{n^2 \cdot pO_2^{0.5}} \tag{6}$$

The law of mass action constants have been experimentally determined.[1] To complete the set of necessary equations, the charge balance has to be added, where ρ represents the local space charge. When we consider local electroneutrality all over the crystal

$$e_0\left(2[V_O^{\bullet\bullet}] + [\mathrm{La}^{\bullet}] - n - 2[V_{Sr}'']\right) = \rho \equiv 0, \tag{7}$$

the locally invariant defect concentrations can be calculated. Fig. 1 shows the concentration of electrons, oxygen vacancies and cation vacancies versus the oxygen partial pressure for donor-doped $SrTiO_3$. According to Eq. (7), the model is limited to the space charge free case.

3. Defect motion

The motion of uncharged particles under a concentration gradient is described by Fick's law,

$$j_{\mathrm{diff}} = -D \frac{\mathrm{d}C}{\mathrm{d}x} \tag{8}$$

where j denotes the flux density, D the diffusion coefficient and C the concentration of the particles. Regarding the diffusion of ionic and electronic species, an internal electrical field E has to be considered as an additional driving force. The flux of a species with the mobility μ and the charge number z under an internal electrical field E is given by Ohm's law

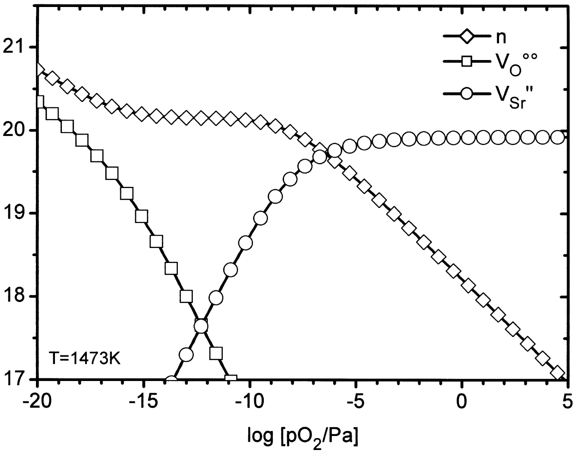

Fig. 1. Calculated point defect concentrations for 1 at.% lanthanum-doped $SrTiO_3$.

$$j_{\text{field}} = \frac{z}{|z|}\mu C E \tag{9}$$

and we find for the net flux:

$$j = j_{\text{diff}} + j_{\text{field}} \tag{10}$$

The ambipolar diffusion[10] takes into account drift and diffusion current in the ambipolar diffusion coefficient. Fig. 2 illustrates the ambipolar concept. In the upper sketch, the diffusion profiles for a faster particle (pos.) and a slower particle (neg.) are introduced. Due to a shift in the centers of charge, a local space charge region is established in the diffusion front and an internal electrical field forms. Assuming a constant dielectric susceptibility ε, the internal electrical field is calculated from the integral over the space charge as follows:

$$E(x) = \frac{1}{\varepsilon}\int_0^x \rho(\xi)\mathrm{d}\xi \tag{11}$$

Note that the conservation of charge over the complete sample has to be satisfied.

Under oxidizing conditions, the concentration of oxygen vacancies can be neglected in donor doped $SrTiO_3$. Then, the local space charge in our model system is determined by:

$$\rho(x) = e_0\left([La^\bullet] - n(x) - 2[V''_{Sr}](x)\right) \tag{12}$$

Hence, the ambipolar concept describes the coupled diffusion of electrons and strontium vacancies. Since both specimen have equal signs of charge, they move in opposite directions. By increase of the oxygen partial pressure (see experimental part), electrons diffuse from the bulk towards the surface, whereas strontium vacancies diffuse from the surface into the bulk. A *negative space charge* establishes in the near-surface region, that is compensated by a positive space charges in the interior. The inner electrical field (in our case negative) slows down the fast particle (n) and accelerates the slow particle (V_{Sr}), since the charge flux of both species becomes equal.

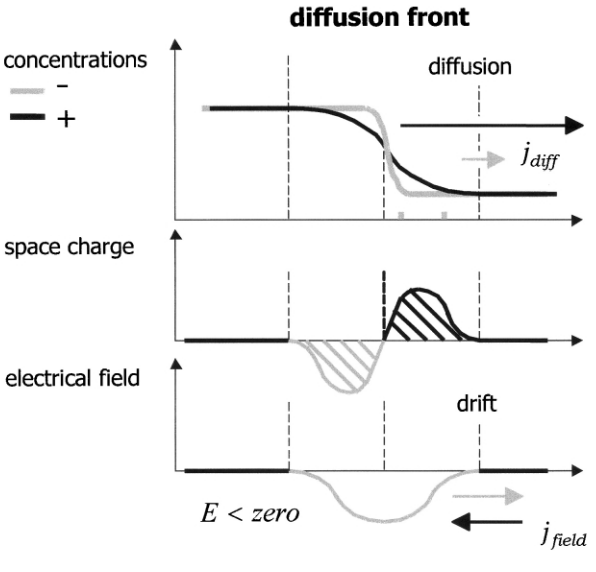

Fig. 2. Scheme of the ambipolar concept.

The next paragraph elucidates point defects under a fixed local charge to estimate the influence of local space charges on the defect concentrations.

4. Defect calculation under local space charge

As for the calculation of point defects in electroneutral regions, we assume the laws of mass action given by Eqs. (5) and (6). In contrast to the assumption in the upper section of the paper, the electroneutrality condition Eq. (7) is replaced by a constant space charge. As a consequence, the sum of all charge carriers including space charges can be rewritten as follows:

$$e_0\left([\mathrm{La}^\bullet] - n - 2[V''_{Sr}] - \frac{\rho}{e_0}\right) = 0 \tag{13}$$

In Eq. (13), we can interpret a negative space charge as a *virtual donor* and a positive space charge as a *virtual acceptor*, respectively. If the absolute value of ρ exceeds the amount of the dopant, we can even inverse the character of the material. Fig. 3 shows the calculated concentration of electrons as well as the concentration of strontium vacancies under electroneutrality and with respect to a space charge of ± 100 As/cm^3.

We observe, that the concentrations of electrons and strontium vacancies are strongly influenced by the presence of space charges and differ several orders of magnitude from the equilibrium values. In case of a positive space charge, the characteristic slopes of acceptor-doped $SrTiO_3$ are found. Since defect concentrations are affected by local space charges and the diffusion of charged defects is regarded as a source for space charges, we postulate a strong interaction the between the formation of defects at the surface and the diffusion process.

5. Defect calculation in the transition state

The numerical simulation tool aix*pert,* developed at our institute, was used to simultaneously calculate the defect concentrations at the surface and the transport of defects by drift and diffusion. We studied the reequilibration of donor-doped $SrTiO_3$ in the high temperature regime after a change from reducing to oxidizing conditions. Fig. 4 shows the concentration profile of strontium vacancies as calculated for a thin slab of about 40 nm thickness. Due to a negative space charge in the near-surface region, the defect concentration exceeds the aspired equilibrium value by nearly two orders of magnitude. During the experimental run, the surface concentration drops to the equilibrium value. The sensor response of the material was calculated from the defect profile of the electrons in order to compare simulation and experimental data.

6. Oxidation experiment

A 1 at.% lanthanum-doped ceramic sample was prepared by the conventional mixed oxide technique. After sintering at 1673 K in wet 2%H_2/98%Ar, the ceramic body revealed an average grain size of 1 μm and a density of 90%. A 4-probe-geometry was chosen for the electrical characterization. Hereby, a dc current was supplied to the outer electrodes by a current source. The voltage drop between the inner electrodes was measured by a high impedance voltmeter. During the experiment, the sample was heated in reducing atmosphere to 1473 K. Then, the atmosphere was changed to air and the evolution of the dc resistivity versus time was monitored. The characteristic shape of the sample resistivity is shown in Fig. 5.

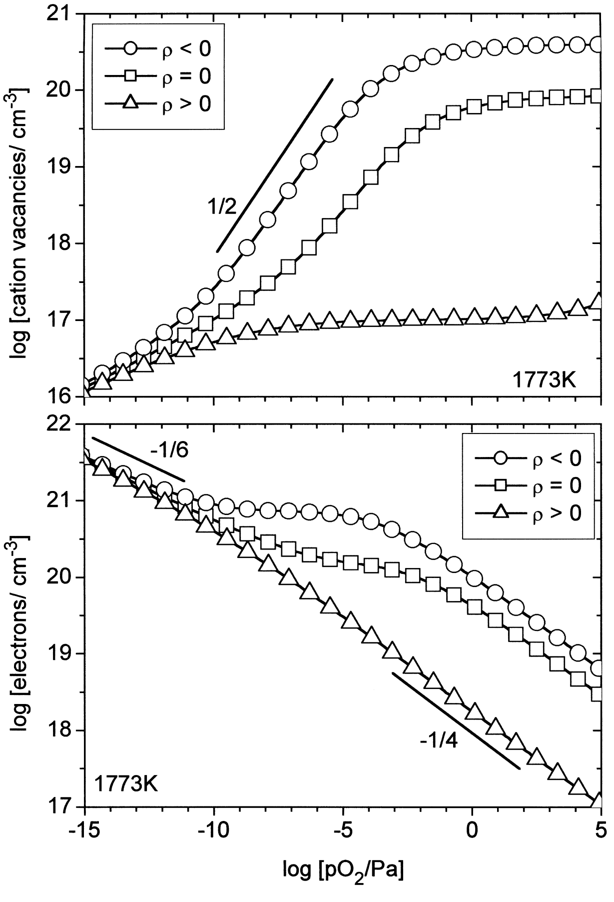

Fig. 3. Influence of a positive and a negative space charge on the concentrations of electrons and strontium vacancies for 1 at.% lanthanum-doped $SrTiO_3$.

Three characteristic regions can be separated. In the short time range, we find a very fast increase of resistivity from 0.1 to 1.5 Ωcm. Due to the exchange delay of the atmosphere, the increase is determined by our setup. The fast increase is followed by a region with a slight change of the resistivity. Finally, the resistivity increases drastically and remains constant.

An interpretation of the entire phenomenon is given by the introduced model. The fast resistivity increase is interpreted as a depletion of electrons in the vicinity of the grain boundary. It is strongly correlated with the very high surface concentration of strontium vacancies at the beginning of the experiment as the new feature of the theory. A comparison with the experimental data confirms the applicability of time variant surface concentration and therefore, the validity of the introduced model.

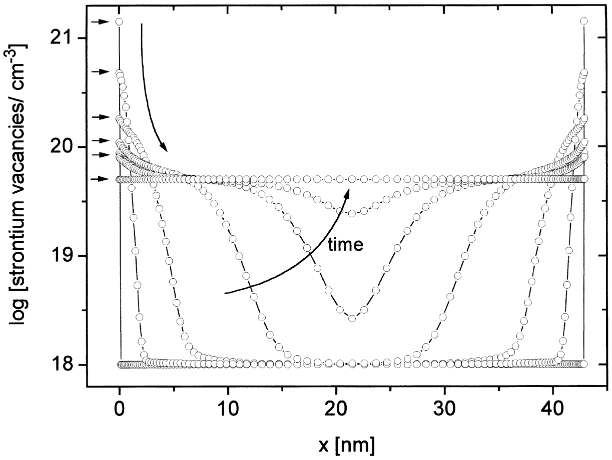

Fig. 4. Profile of strontium vacancies after a change from reducing to oxidizing atmosphere.

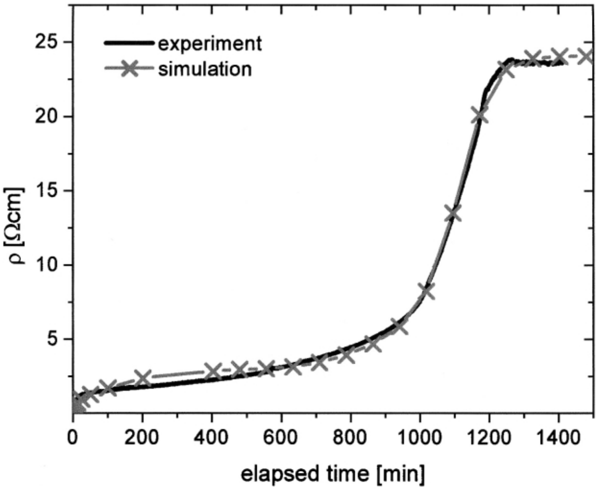

Fig. 5. Simulation versus experiment of the evolution of the sample resistivity during oxidation.

7. Summary and conclusion

It is shown, that the ambipolar diffusion is a source for a local space charge. This space charge significantly influences the defect concentrations. We propose a new approach for the diffusion in oxides, where the surface concentrations are calculated as a function of the local space charge and therefore become time dependent. The applicability of the model is demonstrated for an oxidation experiment.

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