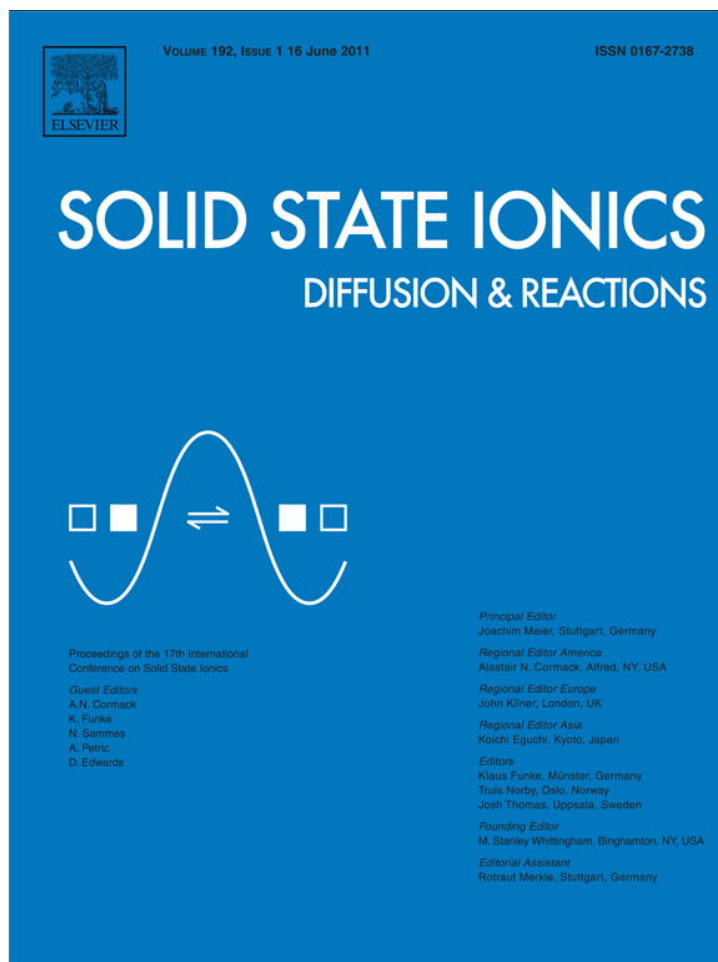


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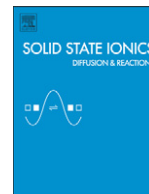


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Water as a source for oxygen incorporation into acceptor doped SrTiO₃ single crystals

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ARTICLE INFO

Article history:

Received 31 August 2009

Received in revised form 8 April 2010

Accepted 3 May 2010

Available online 2 June 2010

Keywords:

SrTiO₃

Oxygen incorporation

Surface exchange coefficient

Perovskite

Water dissociation

ABSTRACT

The possibility of the incorporation of oxygen and deuterium stemming from the dissociation of water into iron doped strontium titanate single crystals with two different iron concentrations (0.13 and 0.013 at.% Fe) has been investigated. Double labeled water (²H₂¹⁸O) was used for Isotope Exchange Depth Profiling. It acts as an incorporation source of ¹⁸O into Fe-doped SrTiO₃(100) single crystals. Total dissociation of the water takes place in the vicinity of the SrTiO₃ surface and both oxygen and deuterium incorporate into the SrTiO₃. The results of the diffusion profile evaluation confirm that oxygen and deuterium migrate independently in the bulk. Oxygen incorporates into the material at high incorporation rates, practically comparable with the ones resulting from an O₂ atmosphere. The interaction of H₂O with SrTiO₃(100) surfaces was further studied with Metastable Induced Electron Spectroscopy and Ultraviolet Photoelectron Spectroscopy. Neither partial dissociation of water molecules nor any significant formation of surface OD groups was observed.

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1. Introduction

SrTiO₃ is a model oxide for electroceramics. It is a typical ABO₃ type perovskite material with remarkable thermal and chemical stability and easy fabricability. As a result of that SrTiO₃ has found applications in a wide range of technologically relevant fields like capacitors, oxygen sensors, dielectrics as well as substrate for superconducting materials. Moreover, depending on the conditions it can show ionic conduction or p- or n-type electronic conduction. The key point that enables one to render this material with a specific conductivity is its suitability for doping with aliovalent dopants without changing its crystal structure [1,2].

The defect chemical basics of this material can be found in the literature [3,4] and in the references therein. For many applications, the diffusion of oxygen vacancies is the key property. It is responsible for the degradation of multilayer capacitors at room temperature [5], but is also the basic principle for the application of SrTiO₃ as resistive high temperature oxygen sensor [6,7], with the analysis of combustion engine exhaust being one important utilisation. The incorporation of oxygen from the gas phase into the crystal is a process involving multiple steps, from the dissociation of oxygen containing molecules in the vicinity of the surface followed by the adsorption at the surface to the oxygen diffusion in the bulk. Recently Merkle and

Maier [8] discussed the oxygen incorporation into oxides on the example of SrTiO₃ as a model material. The rate determining step in the total reaction is the surface interaction.

The most convenient way of studying oxygen incorporation in a crystalline solid is by means of tracer isotope exchange. In this process the oxygen incorporation consists of a surface reaction at the gas solid interface which is characterized by the surface exchange rate constant and a subsequent bulk transport which is characterized by the diffusion coefficient. The objective of this investigation is to see whether different gaseous contaminants and in particular water has an influence on the oxygen incorporation reaction in acceptor doped SrTiO₃. Results for oxygen incorporation from ²H₂¹⁸O sources are reported. The results are supported by measurements with surface sensitive methods like Ultraviolet Photoelectron Spectroscopy (UPS) and Metastable Induced Electron Spectroscopy (MIES).

2. Experimental

Single crystals of SrTiO₃(100) were supplied by CrysTec GmbH (Berlin, Germany). First, each of the two differently doped SrTiO₃ single crystals (0.13 and 0.013 at.% Fe) were cut from one boule each with the dimension of 5 × 5 × 1 mm³ and have been polished down to optical finish with the dimension 0.1 μm.

For the diffusion experiments, all samples were heated at 1000 °C for 24 h in 200 mbar of ¹⁶O₂ in order to heal possible surface defects stemming from the polishing procedure.

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The samples were afterwards equilibrated at the respective temperature for about ten times the estimated subsequent diffusion time in argon, meaning at an oxygen partial pressure similar to the subsequent diffusion from water in order to equilibrate the defect concentration. Two sets of samples were then annealed separately in water atmospheres with different double labeled water ($^2\text{H}_2^{18}\text{O}$ from Campro Scientific, Berlin, Germany) concentration at various temperatures between 850 and 1000 °C. Subsequently, oxygen incorporation processes were studied by Secondary Ion Mass Spectroscopy (SIMS). A detailed description of the procedure for this Isotope Exchange Depth Profiling (IEDP) can be found in [9].

The interaction of H_2O with $\text{SrTiO}_3(100)$ surfaces was further studied with MIES and UPS. Electron spectroscopy is performed in an ultrahigh vacuum (UHV) apparatus with a base pressure of 5×10^{-11} mbar using a hemispherical analyzer (VSW HA100) in combination with a source for metastable helium atoms ($\text{He}^* \ ^3\text{S}_1$) and ultraviolet photons (HeI line). Details on the apparatus used and the theoretical background may be found in [10].

MIES is an extremely surface sensitive technique probing solely the outermost layer of the sample, because the He^+ atoms interact with the surface typically 0.3 to 0.5 nm in front of it. This may occur via a number of different mechanisms depending on surface electronic structure and work function, which are described in detail elsewhere [11–13]. On SrTiO_3 surfaces a special Auger Deexcitation (AD) type interaction occurs [14]: The 2s electron of the impinging He^+ is resonantly transferred into the surface of the sample and localizes at near surface Ti 3d states. Subsequently, a Ti 3d electron fills the hole in $\text{He}^+ \ 1s$ in an interatomic Auger neutralization (AN) process, followed by the emission of an O 2p surface electron carrying the excess energy.

3. Results

Fig. 1 shows the results of a MIES/UPS experiment on a SrTiO_3 surface with low iron content (0.013 at.% Fe). Prior to the experiment, the surface was annealed in UHV at about 970 K for 120 min. to remove contaminations from the surface and to produce oxygen vacancies V_{O} . This is done in order to achieve a sufficient conductivity in the crystal to prevent charge-up during electron spectroscopy. Subsequently, water is offered to the surface at an exposure of 50 Langmuir (L) per spectrum, one Langmuir equals 1.33×10^{-4} Pa s. The

change in the MIES/UPS is shown in a waterfall manner, indicated by the arrow on the right side.

The electron count rate measured during the experiment is plotted versus the electron binding energy, 0 eV corresponds to the Fermi energy. The lowermost spectrum shows the cleaned surface. In UPS, the density of states of the valence band region of SrTiO_3 is detected. Due to the pinning of the Fermi level to the conduction band, the gap energy of 3.2 eV can be recognized, as well as two distinct features at 5 eV and 7 eV. The two features correspond to emission from O 2p-derived orbitals in the surface, the one at 7 eV corresponding to emission from orbitals hybridized with Ti 3d states; the one at 5 eV arises from ionization of non-hybridized orbitals.

He^+ during MIES interact with the surface as described in the experimental section. Only one peak at about 6.5 eV is detectable. It arises from the ionization of non-hybridized O 2p-derived orbitals, because these orbitals are present at the surface due to the broken translation symmetry and protrude much wider into the vacuum as every other state. Therefore He^+ preferentially interact with these states. Thus, the MIES detects the density of the uppermost surface states only.

Fig. 2 gives a clear impression of the concentration of ^{18}O in the bulk of the SrTiO_3 single crystals stemming from the dissociation of the double labeled water. The SIMS diffusion profiles presented in Fig. 3 show oxygen profiles but not any profiles for deuterons at all.

4. Discussion and conclusions

Both the MIES and the UPS spectra (Fig. 1) show the well known valence band of SrTiO_3 as expected from literature [14].

During water exposure no significant change in the density of states of the surface is detected neither in MIES nor UPS even at high exposures up to 1250 L. At the end of the experiment only the development of a very slight shoulder around 11 eV is observed. This structure may be attributed to surface OD groups from the partial dissociation of the surrounding water. Because of the very low count rate of the structure, the coverage of the surface with OD groups must be very small. Because of this, the partial dissociation of water molecules and the subsequent adsorption at the surface must be an ineffective process. Otherwise, MIES would detect much more surface OD groups.

A more detailed investigation of the surface interaction between water and $\text{SrTiO}_3(100)$ may be found in [15]. Besides this slight OD generation on the surface, no further adsorbates could be detected.

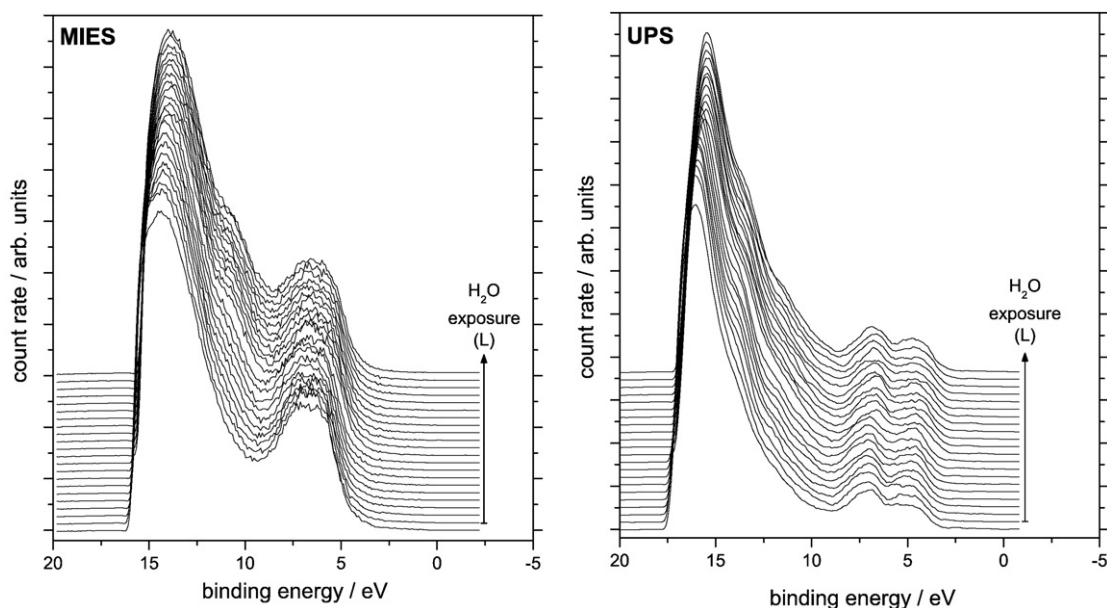


Fig. 1. MIES (left) and UPS (right) spectra of a $\text{SrTiO}_3(100)$ surface with low iron content (0.013 at.% Fe) during exposure to water.

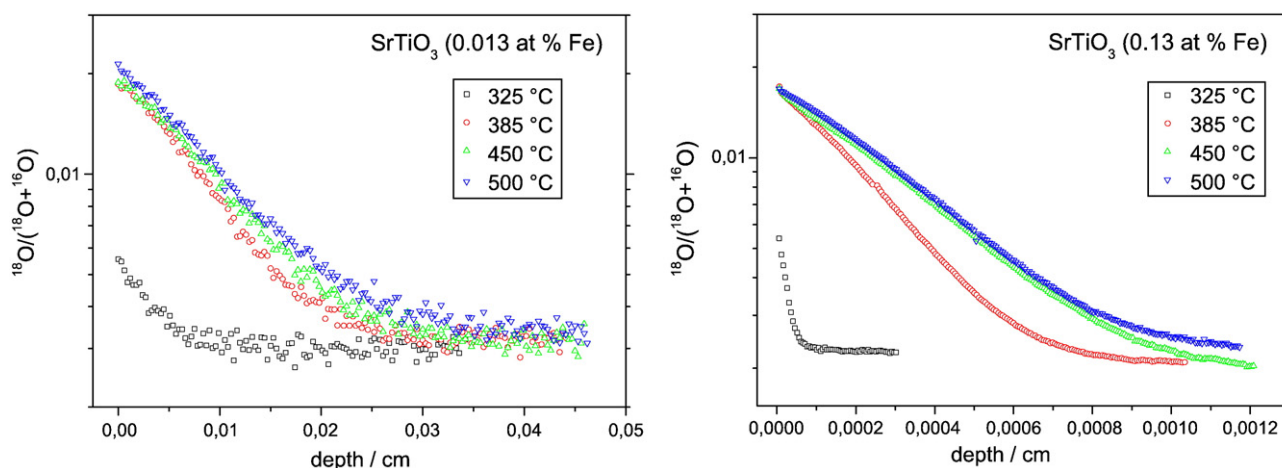


Fig. 2. Depth profiles of oxygen stemming from the dissociation of water in SrTiO₃ single crystals with low iron content (0.013 at.%, left) and high iron content (0.13 at.%, right).

The results of the diffusion profile evaluation (Fig. 3) confirm that ²H₂¹⁸O acts as an incorporation source of ¹⁸O into the Fe-doped crystals and that oxygen and deuterium migrate independently in the bulk. This oxygen incorporates into the material at high incorporation rates, practically comparable with the ones resulting from an oxygen atmosphere [18].

Surface hydrogen and surface oxygen are not necessarily detectable by means of MIES/UPS leading to the assumption that a total dissociation of the water in the vicinity of the SrTiO₃(100) surface is the source of the ¹⁸O. After dissociation both oxygen and deuterium may incorporate into the SrTiO₃ and migrate independently in the bulk.

The low concentration of deuterons in the depth profile in Fig. 3 is a confirmation that ¹⁸O-ions and deuterons migrate in the SrTiO₃ bulk independently, otherwise parallel depth profiles should be found. This can indicate one or both of the two following possibilities:

1. The deuterons do not incorporate into SrTiO₃ to the same extent as oxygen does, meaning that a recombination of the deuterons to ²D₂-molecules on the SrTiO₃ surface occurs, followed by their desorption into the gas phase.
2. The deuterons are incorporating and diffusing much quicker than ¹⁸O-ions so that they can reach the surface again, confirming that ¹⁸O-ions and deuterons migrate in the SrTiO₃ bulk independently.

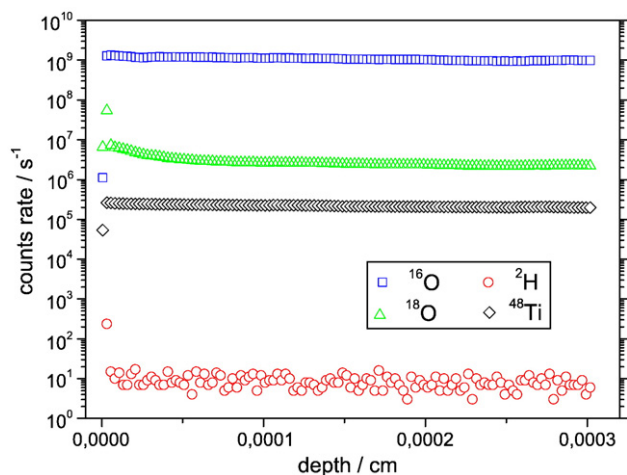


Fig. 3. Raw data of the depth profiles in SrTiO₃ single crystals doped with 0.13 at.% Fe at 500 °C from the dissociation of double labeled water. It is obvious that in contrast to the ¹⁸O there is no deuterium diffusion profile in the bulk. The signal is practically as low as the background.

Our results up to now confirm the second possibility and thus the findings of Kreuer [16] that deuterium migrates much quicker than oxygen in SrTiO₃. That means it migrates as ²D⁺ and not in the form of OD groups.

Based on the MIES/UPS results as well as the SIMS diffusion profiles we assume that a total dissociation of the water takes place in the vicinity of the SrTiO₃(100) and that subsequently both oxygen and deuterium incorporate into the SrTiO₃ and migrate independently in the bulk. This assumption is supported by the results of the evaluation of the SIMS diffusion profiles, where we found oxygen profiles (Fig. 2) but not any profiles for deuterium at all (Fig. 3). In the case of coupled migration of deuterium together with oxygen one would expect parallel diffusion profiles for oxygen and deuterium which is not confirmed with our results. Furthermore, we do not observe any significant formation of surface OD groups from the partial dissociation of water with our MIES spectrometer. Because of this, diffusion of OD groups into the bulk seems unlikely.

We can conclude that water acts as a source for oxygen incorporation into SrTiO₃ and because of the model character of SrTiO₃ probably in other perovskite materials as well. Oxygen incorporates into the SrTiO₃ single crystal bulk at high incorporation rates [17], practically comparable with the ones resulting from an O₂ atmosphere. The influence of the dopant content and of the temperature on the oxygen diffusion in the crystal is discussed in detail elsewhere [18]. Based on these findings, we can state that attention has to be paid when such materials are used in humid atmospheres for example as sensor materials.

Acknowledgements

We gratefully acknowledge the financial support by the Deutsche Forschungsgemeinschaft (DFG) under contract numbers Ar 248/3-2 and Ma 1893/9-2.

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