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Novel Features of Water Incorporation in Oxides Revealed by *in situ* Local Absorption Spectroscopy

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Fe-doped $\mathrm{SrTiO_3}$ is a model mixed conducting perovskite offering the perspective to develop an accurate description of thermodynamics and kinetics of water incorporation, since thermodynamic parameters in oxygen incorporation and intrinsic redox reactions are well established [1]. Water incorporation into the oxygen vacancies of Fe-doped $\mathrm{SrTiO_3}$ was found to occur to a small but nonzero degree [2]. In acceptor-doped oxides with predominant oxygen vacancies water incorporation fills the vacancies with protonic defects $\mathrm{OH_O^{\bullet}}$ in a pure acid-base reaction (Fig. 1a). The purpose of the present study is to investigate the kinetics of water incorporation in Fe-doped $\mathrm{SrTiO_3}$ involving redox as well as acid-base processes owing to the presence of three charge carriers, $\mathrm{V_O^{\bullet\bullet}}$, $\mathrm{OH_O^{\bullet}}$, $\mathrm{h^{\bullet}}$ (Fig. 1b).

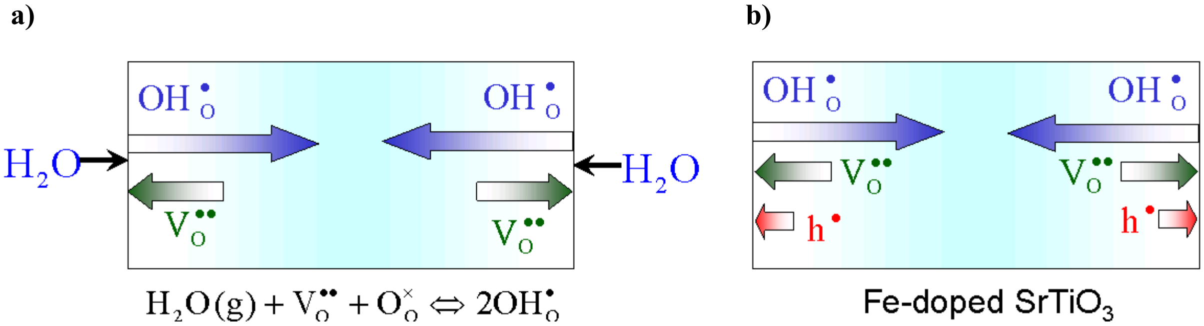

Fig. 1: Scheme of water incorporation into $\mathrm{SrTiO_3}$: a) pure acid-base mechanism, b) combined acid-base and redox process

In order to resolve the complex kinetics with contributions from surface reaction as well as bulk diffusion, space-resolved optical absorption measurements were performed on a 6 × 6 × 1 $\mathrm{mm^3}$ sized Fe-doped $\mathrm{SrTiO_3}$ single crystal [3]. In these experiments the large crystal faces are sealed, thus the in-diffusion of the different charge carriers from the edges can be followed by space-resolved measurements of the $\mathrm{Fe_{Ti}^{x}}$ absorption which serves as an indicator also for all other point defect concentrations. An example is shown in Fig. 2.

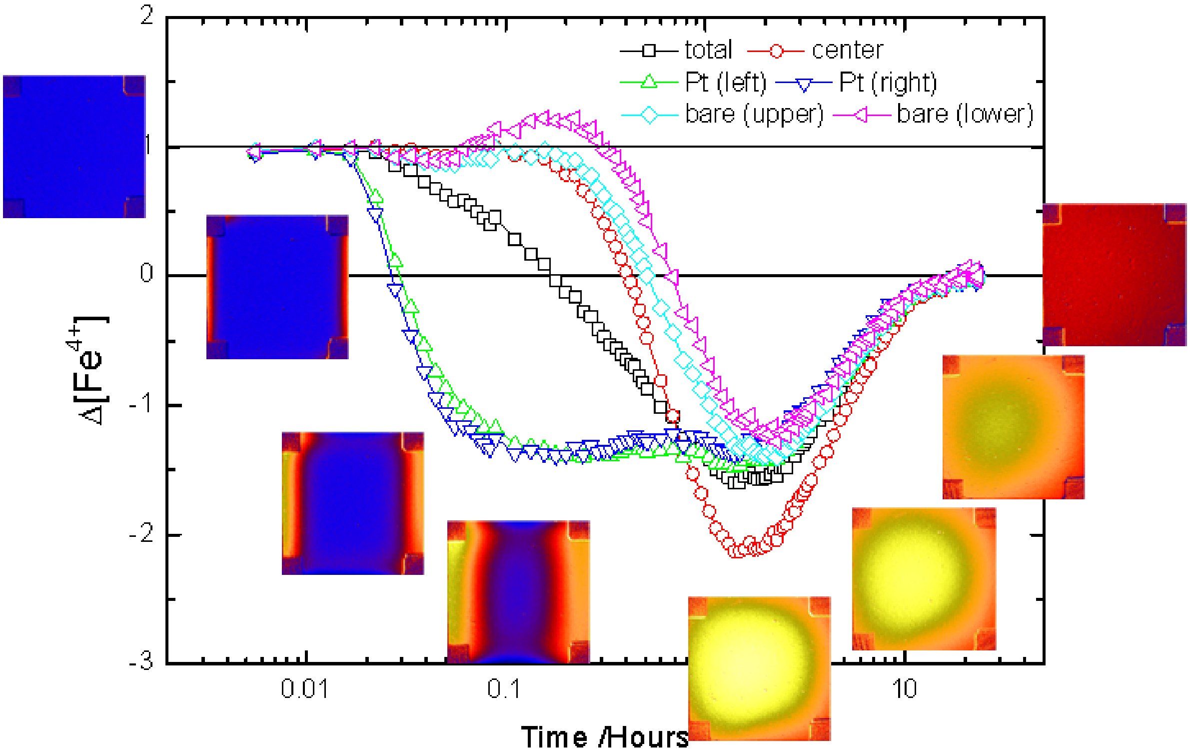

Fig. 2 Insets: time-dependent and space-resolved optical absorption in Fe-doped $SrTiO_3$ after a $p(H_2O)$ increase from 4 to 20 mbar in oxygen at 500 °C ; false-color representation. The left and right edges of the sample are coated with a porous Pt layer facilitating the water dissociation reaction $H_2O \rightleftharpoons 2\ H^+ + 1/2\ O_2 + 2\ e^-$. Colored symbols: Fe_{Ti}^x concentration in selected regions, black squares: averaged over whole sample

Directly after an increase in $p(H_2O)$, a zone of lower Fe_{Ti}^x concentration starts to extend into the sample from the left and right edges. After about 1 hour the whole sample is in an "over-reduced" state due to the fast incorporation of protons and electrons emerging from the dissociation of water at the surface according to $H_2O \rightleftharpoons 2\ H^+ + 1/2\ O_2 + 2\ e^-$. Because of the much slower oxygen diffusion in $SrTiO_3$, the following oxygenation $1/2\ O_2 + V_O^{\cdot\cdot} \rightleftharpoons O_O^x + 2\ h^{\cdot}$ occurs on a significantly longer time scale. According to the defect-chemical model [2], the complete water incorporation process leads to a slight overall decrease of the Fe_{Ti}^x concentration.

The *in situ* optical absorption spectroscopy not only unambiguously indicates that the oxide was strongly reduced first and then re-oxidized to the final equilibrium. It also reveals more subtle features of water incorporation such as predominant diffusion control (*i.e.*, fast surface reaction) for the hydrogen incorporation at the Pt coated edges, while the bare surface exhibits much slower kinetics for this combined acid-base and redox reaction.

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