

Point Defects and Diffusion in Oxides

J. Shi* and K.-D. Becker

Abstract. Electronic and ionic defects are unavoidable elements of structural disorder in oxide materials resulting from nonstoichiometry or impurity/doping ions. Many point defects involving electrons or transition metal ions give rise to optical absorption, providing a probe to study defect chemistry and transport properties in these materials. We present the application of optical in-situ spectroscopy to the investigation of defects and defect-related processes at elevated temperatures in N-doped titania films and Li-deficient lithium niobate.

Key words: point defects, diffusion, optical spectroscopy, N-doped TiO_{2-δ} thin film, lithium niobate.

I. INTRODUCTION

Nonstoichiometry or doping/impurity ions in oxides produce electronic and ionic defects on sublattices in the crystal structure. These point defects play a decisive role in diffusion processes in oxide materials. Information on point defects in equilibrium and defect dynamics is of importance for the understanding of reactivity, degradation mechanisms of functional materials as well as for the development of new materials with improved transport properties.

Due to the sensitivity to electronic transitions of ions and defects, optical spectroscopy in the UV-vis-NIR range is one of the versatile spectroscopic techniques for the study of point defects, reaction kinetics and diffusion, in particular, under in-situ conditions.

II. MATERIALS AND METHODS

N-doped TiO_{2-δ} thin films of about 1 μm were prepared on sapphire substrates using pulsed laser deposition. The films show an anatase phase with strong optical absorption in the visible and near IR range. The films were cut into a suitable size and used as absorbers in the present study. In the case of congruent lithium niobate, thin sections were cut from a crystal wafer and polished on both sides and used as optical absorbers. The experimental setup for in-situ optical measurements is schematically shown in Fig. 1, for details see elsewhere [1].

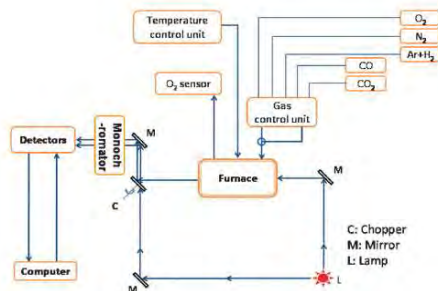


Fig. 1. Schematics of optical in-situ spectroscopy.

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III. RESULTS AND DISCUSSION

A. Oxidation kinetics of N-doped TiO_{2-δ} thin film

Fig. 2a shows a series of optical absorption spectra of a N-doped TiO_{2-δ} thin film recorded at 600 °C during oxidation in O₂ atmosphere. The defect-induced absorption in the visible and NIR region decreases with time in the course of oxidation. After about 40 min, the film is completely oxidized showing a flat, absorption-free spectrum superimposed by interference fringes due to multiple reflections at the sample's interfaces. Another feature observed in the oxidation process is the blue-shift of the optical band gap from about 2.5 eV for the as-prepared, reduced state to about 2.9 eV for the fully oxidized thin film (600 °C). The oxidation kinetics of the N-doped TiO_{2-δ} thin films can be quantitatively analyzed on a basis of parabolic rate law provided that the concentration of electron-related defects in oxidized film is close to zero compared to that in the reduced thin film. Therefore, a correlation between absorbance, A and oxidation rate constant, k_p can be derived as

$$[(A_t - A_0)/(A_\infty - A_0)]^2 = 2k_p t / d^2. \quad (1)$$

Here, A_t represents the absorbance at time t , A_0 and A_∞ are the absorbance of the absorber before ($t = 0$) and after the completion of oxidation ($t = \infty$). d is the thickness of the absorber. As seen in Fig. 2b, the time dependence of $[(A_t - A_0)/(A_\infty - A_0)]^2$ exhibits a fairly linear behavior with a rate constants k_p of $(2.53 \pm 0.02) \times 10^{-16} \text{ m}^2/\text{s}$ at 600 °C.

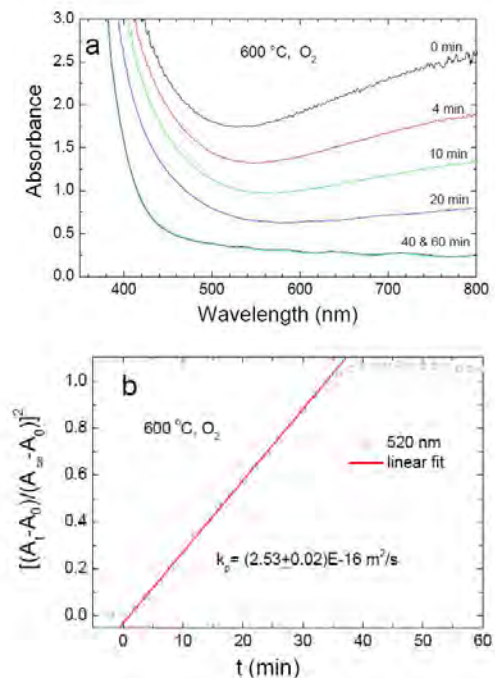
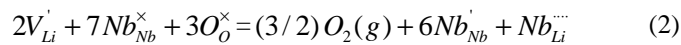


Fig. 2. Time dependent optical absorption spectra (a) and oxidation kinetics monitored at 520 nm (b) at 600 °C of a N-doped TiO_{2-δ} thin film.

B. Redox kinetics of congruent lithium niobate

Chemical reduction of lithium deficient lithium niobates induces coloration of the initially transparent crystals [2, 4] because of the optical absorption of electronic defects, namely, electron polarons. At room temperature and low temperatures, the optical absorption spectra are dominated by absorption of bipolarons, $(Nb'_{Nb}Nb''_{Li})^{\cdot\cdot}$, which is an association of small polarons, i.e. electrons trapped on regular Nb^{5+} ions, Nb'_{Nb} or antisite Nb^{5+} ions, Nb''_{Li} [2]. At elevated temperatures, the optical absorption spectra of reduced lithium niobate are dominated by a band due to free electron polarons centered at about 7500 cm^{-1} (0.9 eV), Fig. 3a. As seen in Fig. 3b its intensity follows a power law dependence on oxygen activity $(a_{O_2})^m$ with a parameter $m = -(0.23 \pm 0.01)$, Fig. 3b. This is in good agreement with the reduction model,



which predicts that $[Nb'_{Nb}] \propto [V'_{Li}]^{1/6} a_{O_2}^{-1/4}$.

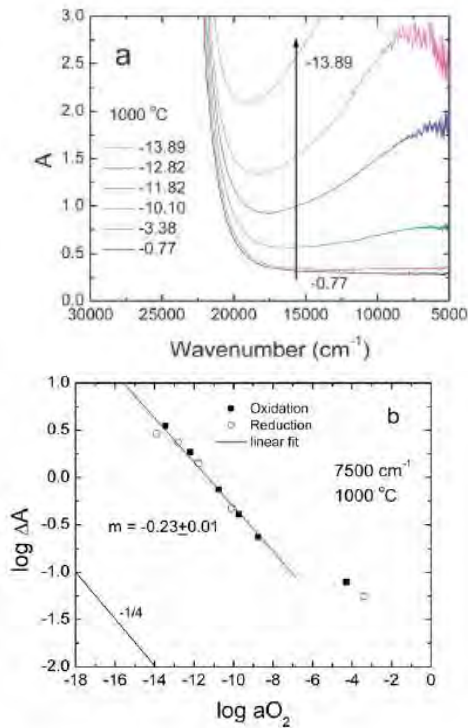


Fig. 3. Optical absorption spectra at various oxygen activities (a), and oxygen activity dependence of free electron polaron absorption (b) at 1000 °C in congruent lithium niobate.

Fig. 4 represents a typical redox process monitored at 15390 cm^{-1} in lithium niobate upon sudden changes in oxygen activity. The data have been fitted according to the diffusion model as shown in (3), and the quality of the fits indicates that the reduction and oxidation processes are diffusion-controlled at the present experimental conditions.

$$\frac{A_t - A_\infty}{A_0 - A_\infty} = \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(-\frac{(2n+1)^2 \pi^2}{d^2} \tilde{D} \times t\right) \quad (3)$$

Here A_t , A_0 , A_∞ and d are defined as in (1), \tilde{D} is the

chemical diffusion coefficient for the underlying ambipolar diffusion process.

Chemical diffusion coefficients, \tilde{D}_{ox} and \tilde{D}_{red} , obtained for oxidation and reduction are nearly equal and give a mean value of about $1.1 \times 10^{-11} \text{ m}^2/\text{s}$ at 1000 °C . Considering that the electronic transference number of lithium niobate is close to 1 under reducing conditions [3], the chemical diffusion processes are dominated by lithium vacancy diffusion. Therefore the lithium vacancy diffusion coefficient can be obtained from \tilde{D} if the lithium vacancy concentration is known, e. g., $D_{V_{Li}}$ has been determined to be about $1.7 \times 10^{-11} \text{ m}^2/\text{s}$ at 1000 °C in congruent lithium niobate [1].

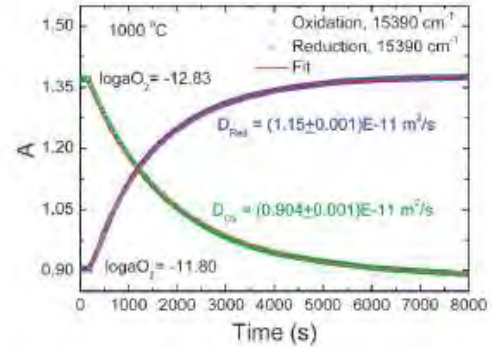


Fig. 4 Kinetics of typical redox processes at 1000 °C in lithium niobate upon sudden changes in oxygen activity between $\log a_{O_2} = -12.8$ and $\log a_{O_2} = -11.8$. The solid lines represent the best fits according to the diffusion model, (3).

IV. CONCLUSIONS

UV-vis-NIR spectroscopy at elevated temperatures is a powerful technique to study point defects and diffusion in oxide materials under in-situ conditions. It has been demonstrated that by using suitable techniques one can study defects in equilibrium as well as defect-related kinetic processes. The oxidation rate constant in N-doped $TiO_{2-\delta}$ thin films was found to be about $(2.53 \pm 0.02) \times 10^{-16} \text{ m}^2/\text{s}$ at 600 °C . The diffusion coefficient of lithium vacancies, V'_{Li} was determined to be about $1.7 \times 10^{-11} \text{ m}^2/\text{s}$ at 1000 °C from the redox kinetic processes in congruent lithium niobate.

ACKNOWLEDGMENT

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