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Investigating Diffusion Processes in Solids Under *in situ* Conditions Using High-Temperature Optical Spectroscopy

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Diffusion processes have always played an important role in solid state research as they provide the quantitative basis for the fundamental understanding of the reactivity of solids. Today, various methods are available to investigate the transport of matter and charge in solids such as tracer diffusion, impedance spectroscopy, or NMR spectroscopy [1]. In addition, also optical spectroscopy is a powerful tool for the study of kinetic processes in solids. Heterogeneous as well as homogeneous reactions in both, crystals and powders can be investigated at high temperatures and variable partial pressures of oxygen.

The present work shows how diffusion processes can be studied at elevated temperatures and various low oxygen activities by the use of optical transmission spectroscopy. A specially designed set-up is used to perform measurements at temperatures up to 1573 K and different CO/CO_2 gas mixtures to control the concentration of defects in crystals. Our set-up also allows quick changes of the gases at isothermal conditions.

Diffusion processes in Co_2SiO_4 single crystals have been analyzed in detail. The single crystals are dark purple colored. According to its orthorhombic structure, anisotropic diffusion can be expected for the cobalt ions located in the two different cation sites M1 and M2 of the olivine structure. Time and temperature dependent measurements using polarized light at a fixed wavelength of 430 nm for all three directions give evidence of anisotropic properties.
For studying the kinetics of the redox processes in Co_2SiO_4, rapid jumps of up to two orders of magnitude in oxygen activity have been performed in a systematic way. The incorporation and removal of oxygen leads to the formation and elimination of defects in the crystal lattice. As major defects divalent vacancies in the cobalt lattice and Co^{3+} on Co^{2+} sites as electron holes have to be taken into consideration. The formation of defect species comes along with significant changes in optical absorbance. With higher $a(O_2)$, the concentration of defects rises which can be observed by an increase in optical absorbance. At lower activities defect concentration decreases accompanied by a decrease in optical absorbance. A typical $a(O_2)$-jump induced relaxation experiment is illustrated in Fig. 1, where $a(O_2)$ is varied from $\lg a(O_2) = -11.15$ to $\lg a(O_2) = -12.25$.

Because of the presence of cobalt-ions with different oxidation states due to oxidation and reduction processes, diffusion is composed of a coupled flux of cation vacancies and holes. Since optical absorbance is proportional to the concentration of the absorbing defects, chemical diffusion coefficients can be calculated from the data thus obtained using the one-dimensional solution of the diffusion equation [2].

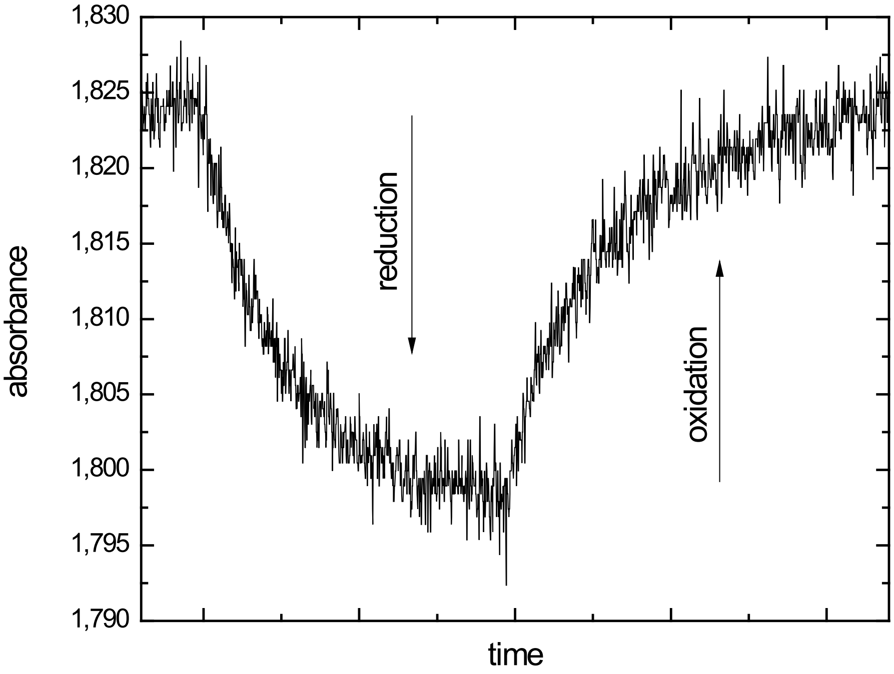

Fig. 1 Relaxation experiment of Co_2SiO_4 due to a jump of $a(O_2)$ at $T = 1278$ K.

Finally it has been ascertained that the diffusion along *c*-axis is fastest, followed by *b*- and *a*-axis. Activation energies in the temperature range of 1023 - 1278 K show smallest values for diffusion along *c*-axis which is in agreement with former works on diffusion processes in olivine systems [3].

References

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