Electrical Conductivity Relaxation Experiments on Single Crystalline Cobalt Silicate Co_2SiO_4 by using Impedance Spectroscopy

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As a major component of the upper Earth's mantle, olivines like $(Fe_xMg_{1-x})_2SiO_4$ are known to conduct the current associated with the Earth's magnetic field. Therefore it is of interest to understand the microscopic mechanisms of transport and the defect chemistry of these materials. Due to its orthorhombic crystal structure (space group P*bnm*) the transport properties show a distinctive anisotropy. In these investigations on the anisotropic transport properties of olivines the isostructural cobalt containing model system Co-olivine (Co_2SiO_4) is used.

Four-point impedance spectroscopic measurements on single crystalline Co_2SiO_4 were performed. The crystals were grown in cooperation with the Dieckmann group of Cornell University by a floating zone method in an image furnace [1] from Co_2SiO_4 powder prepared by a sol-gel synthesis. The samples for impedance spectroscopy are right angular parallelepipeds (approx. $2 \times 2 \times 10$ mm³), that were cut out of the crystals with the longest axis parallel to one of the main crystal axes.

The electrical conductivity σ was then measured parallel to the main crystal directions [100], [010] and [001] to characterize its anisotropy and its oxygen partial pressure dependence at different temperatures. All measurements were performed within the thermodynamic stability field of Co_2SiO_4 between 600 °C and 1200 °C in the range $-12 < \lg p(O_2) < 0$. The below defect model [2] is used to describe the oxygen partial pressure dependence of the electrical conductivity σ.

$$2O_2(g) + 8Co_{Co^{2+}}^x \rightleftharpoons 2V_{Co^{2+}}'' + 2V_{Si^{2+}}'''' + 4O_{O^{2-}}^x + 8Co_{Co^{2+}}^\bullet \tag{1}$$

Because holes are supposed to be the dominant electronic charge carriers in this compound, the conductivity σ is correlated with the concentration of holes.

$$\sigma \propto [Co_{Co^{2+}}^\bullet] \propto p(O_2)^{\frac{1}{n}} \tag{2}$$

The expected value for *n* from the corresponding law of mass action is 5.5. The previous results for the oxygen partial pressure dependence are displayed in Table 1 and in Fig. 1.
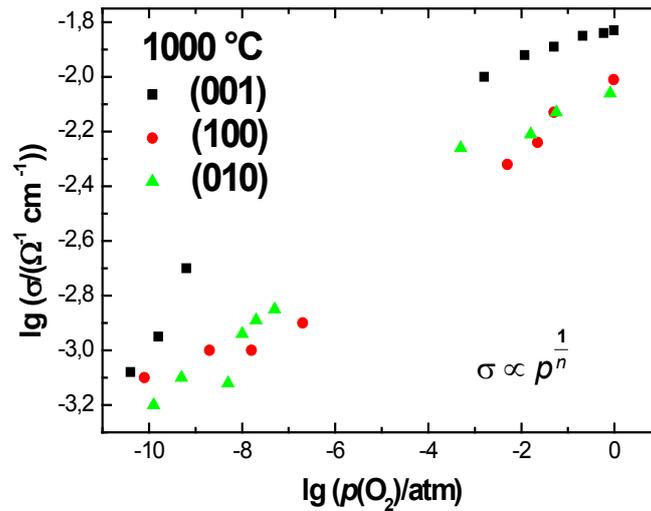
n	$T = 1000\ °C$	$T = 1100\ °C$	$T = 1200\ °C$
(100)	8.7 ± 0.6	–	–
(010)	8.2 ± 0.5	–	$5,6 \pm 0,2$
(001)	8.5 ± 0.4	$5,1 \pm 0,2$	–
(101)	$T = 1270\ °C$	$n = 7.7$ [2]	

Fig. 1 and **Table 1:** Oxygen partial pressure dependence of the conductivity of Co_2SiO_4.

Additionally, electrical conductivity relaxation experiments (ECR) were performed by rapidly changing the oxygen partial pressure in well defined steps. If the relaxation process is limited by the diffusion of cobalt vacancies and holes into the bulk, the change of the conductivity from σ_0 to σ_∞ can be described by a diffusion model [3]. Thus, it is possible to calculate chemical diffusion coefficients from the in situ measurement of the electrical conductivity. In this case, diffusion takes only place perpendicular to the axis of the conductivity measurement, because two sides of the brick-shaped sample are covered by electrodes. The time evolution $\sigma(t)$ has been analyzed by the below two-dimensional diffusion model, where a and b represent the edges of the rectangular cross-section of the sample.

$$\frac{\sigma(t)-\sigma_\infty}{\sigma_0-\sigma_\infty}=\left(8/\pi^2\right)^2 \sum_{m,n=0}^{\infty} \frac{e^{-\tilde{D}(t+t_0)\frac{\pi^2}{4}\left(\frac{(2m+1)^2}{a^2}+\frac{(2n+1)^2}{b^2}\right)}}{(2m+1)^2(2n+1)^2} \tag{1}$$

Therefore, the calculated diffusion coefficient represents a superposition of the diffusion parallel to a and b. Diffusion coefficients at 1000 °C are illustrated in Fig. 2, where the x-error bar represents the change of the oxygen partial pressure during the relaxation process. The orientation given there is the direction of conductivity measurement, whereas the diffusion coefficients from optical spectroscopy [4,5] are for the diffusion parallel to one of the main crystal axes a, b and c. The results from ECR are within the same order of magnitude, although they represent a superposition for the diffusion perpendicular to the axis of the conductivity measurement.
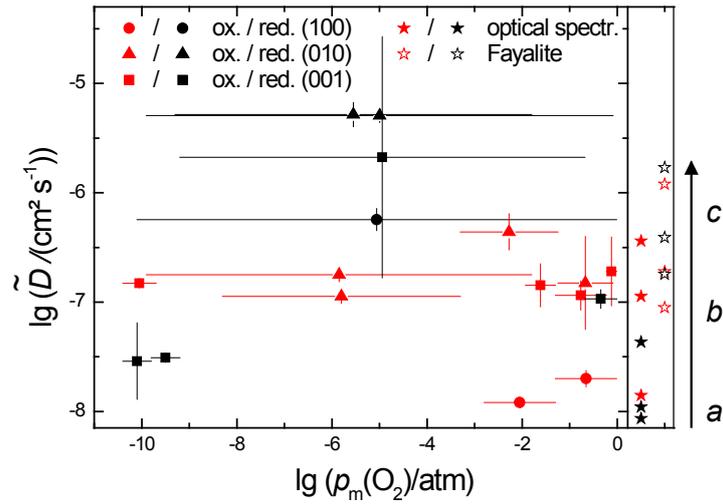
Fig. 2 Chemical diffusion coefficients in Co$_2$SiO$_4$ from ECR at 1000 °C. The given orientation is the axis of conductivity measurement and the *x*-error bar represents the change of the oxygen partial pressure. The data from optical spectroscopy are for 950 °C (Co$_2$SiO$_4$) [5] and for 1130 °C (fayalite, Fe$_2$SiO$_4$) [4].

References

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