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Formation of Structural Bonded OH-Groups in Fused Mullite – Influence of Grain Boundaries on the Diffusion Detected by Transmission Micro-IR Spectroscopy

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Polished plane-parallel sections (1 mm in thickness) of fused mullite ($2Al_2O_3 \cdot 1SiO_2$) were exposed to a slowly flowing (≈ 100 ml/min) water vapor containing atmosphere ($H_2O/O_2 = 20/80$) at a temperature of 1670 °C for 1.5, 3, 6 and 12h, respectively. The water vapor experiments on fused mullite were carried out together with experiments on mullite single crystals reported earlier [1]. All samples were investigated by means of optical microscopy and transmission micro-infrared spectroscopy (Bruker IFS 88 with an attached Bruker IRscope II) before and after the experiments. Two effects were observed: surface corrosion characterized by the formation of α-alumina on the mullite surface and the formation of structurally bonded OH groups in the bulk due to diffusion processes. The surface corrosion effects as well as diffusion profile analysis were described in detail for mullite single crystals earlier [1,2]. In this work results obtained from the fused mullite samples showing the influence of grain boundaries on the diffusion process are reported.

Transmission micro-IR-spectroscopy reveals the formation of structurally bonded OH-groups in fused mullite after water vapor treatment. The IR-spectra of the treated samples show, in comparison to the IR-spectra of the as received samples, additional peaks in the range between 3200 and 3700 cm^{-1} which are characteristic for OH-groups. Lorentz-profile-analysis was used for deconvolution of the IR spectra. A good fit for the IR-spectra measured with the electrical field vector polarized along the crystallographic a-axis of mullite ($E \parallel a$) was obtained using four peaks (Fig. 1). The results of the profile-analysis are given in Table 1. The IR-spectra measured for polarizations $E \parallel b$ und $E \parallel c$ are significantly different [3,4]. This anisotropy shows that the OH-groups are structurally bonded in mullite because an orientation depending absorption could not be due to fluid inclusions. The peak intensities are correlated to the absolute OH-content in the sample and increase with the exposure time. Further IR-measurements were carried out along cross sections of the treated samples (Fig. 2). A xy-stage was used to allow the measurement of data points with constant distances to each other. The distance between two data points was set to 0.1 mm. A slit aperture of 0.1 × 0.6 mm in size was used. All spectra were measured with the electrical field vector polarized along the crystallographic a-axis. The ab-

Table 1: Results of the profile analysis

peak #	peak position (cm^{-1})	peak intensity (cm^{-1})	peak width (cm^{-1})	peak area (cm^{-1})
1	3338	0.095	135.2	22.83
2	3448	0.385	102.2	61.78
3	3547	0.256	62.5	25.17
4	3599	0.302	66.6	31.63

sorption intensity was measured at 3448 cm^{-1} (maximum OH-peak # 2, Tab. 1) for each data point and plotted versus the distance of the measured point to the outer rim of the sample cross section to obtain an OH-concentration profile. The resulting profiles obtained from the data points measured along the marked lines on the cross section of the fused mullite plate after water vapor treatment for three hours are given in Fig. 2 (profile 1 and 2). Profile 1 shows that the amount of OH-groups in the bulk decreases from the outer rim to the middle of the sample cross section. Profile 2 was measured across two grain boundaries and reveal that the grain boundaries act like surfaces in relation to the diffusion process. The amount of OH-groups increases near the grain boundaries like observed at the outer rims of the sample. The mechanism which leads to the formation of OH-groups could be explained by proton diffusion into mullite to substitute lattice cations (Si^{4+} or Al^{3+}), *i.e.*, via cation vacancies [4]. From mullite single crystal data a diffusion coefficient in the range between 8×10^{-8} cm^2/s and 2.3×10^{-7} cm^2/s was estimated for the diffusion process leading to the formation of OH-groups at 1670 °C [1,3]. However, it may be noted that the tracer diffusion of lattice cations (^{30}Si, ^{26}Al, ^{18}O) in mullite was reported to be at least four magnitudes slower [5]. Further experiments are nessecary to clarify the diffusion mechanism in detail.

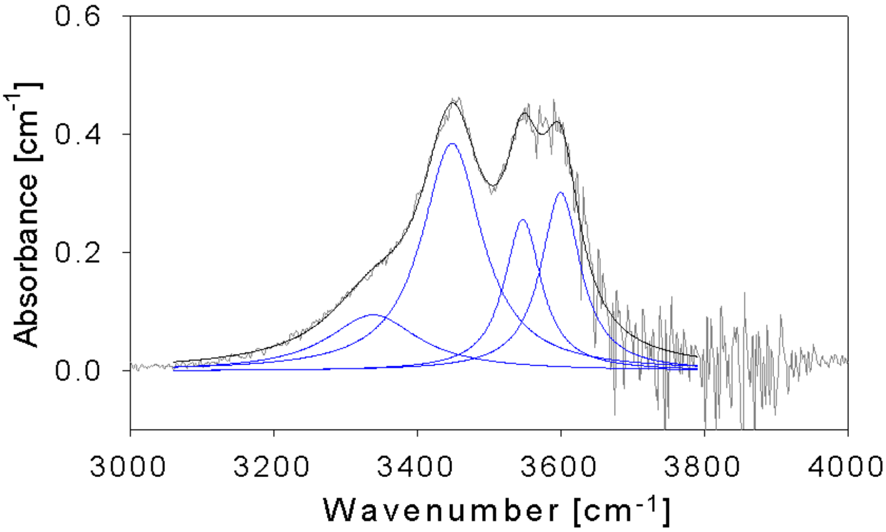

Fig. 1 IR-spectrum of a fused mullite after water vapor treatment (12 h).

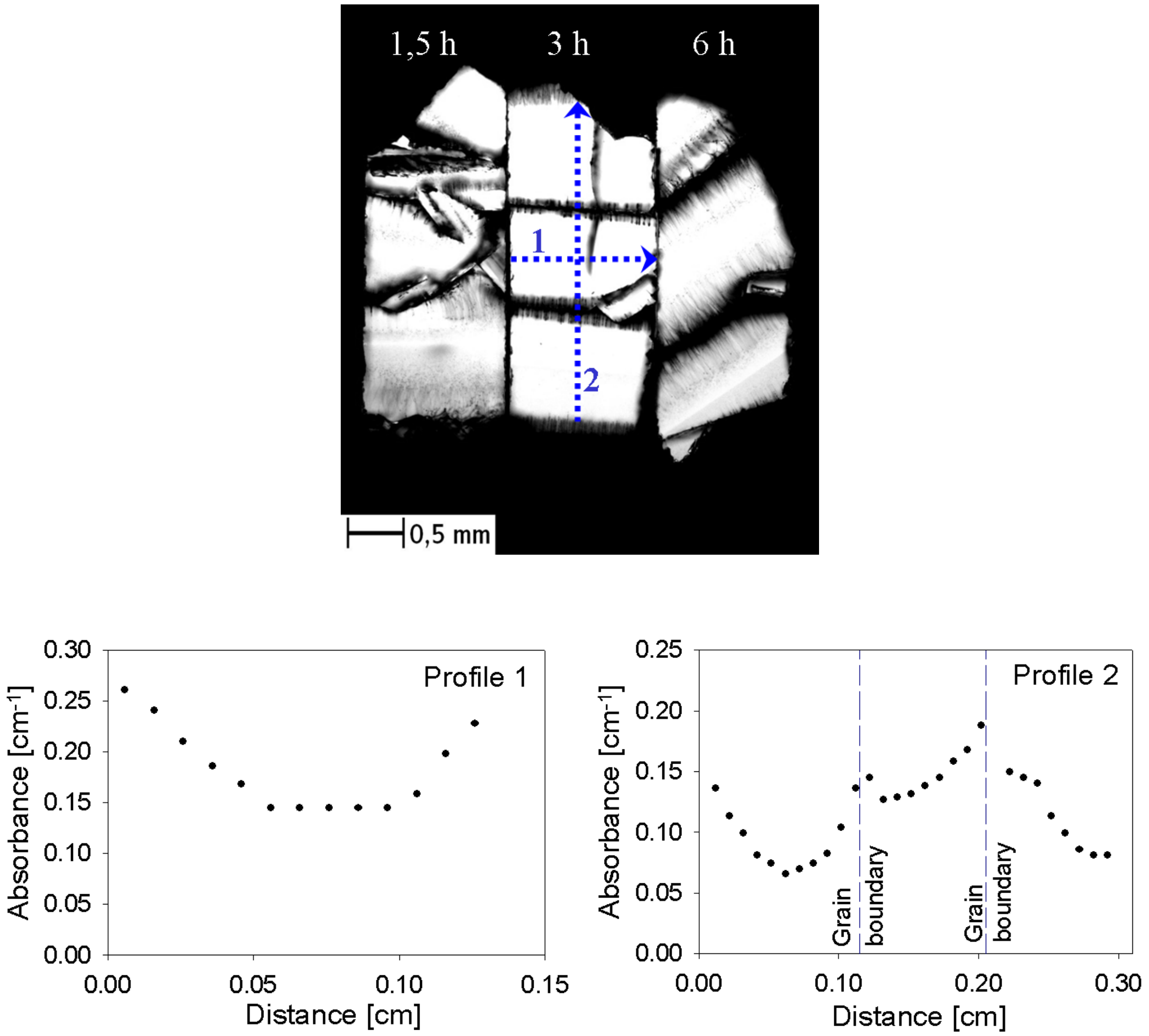

Fig. 2 Optical micrograph showing the cross sections of fused mullite samples after water vapor treatment (top). The OH-concentration-profiles (bottom) are obtained from the data points measured along the marked lines by means of IR spectroscopy.

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