

Hydrogen in α -alumina and water softening of polycrystals and of sapphire between 600°C and 1000°C

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Trace hydrogen impurities influence the physical and chemical properties of silicate minerals. Hydrogen defects reduce the plastic yield strengths of quartz and olivine (Kronenberg, 1994; Kohlstedt *et al.*, 1996) and they increase rates of oxygen diffusion and Al/Si exchange in feldspars (Farver and Yund, 1990). Hydrogen impurities may similarly affect the properties of oxides and other non-silicate minerals, as suggested by early studies by Heuer *et al.* (1971), who reported water weakening of fine-grained (2 μm) aluminum oxide at 1200°C and 1400 MPa confining pressure. In this study, we revisit the mechanical properties of α -Al₂O₃ in the presence of water, and examine the uptake of hydrogen impurities by single crystals and polycrystals at temperatures of 600–900°C and $\text{PH}_2\text{O} = 1500$ MPa.

Experimental techniques

We used three classes of alumina starting materials: Verneuil grown sapphire crystals (provided by RSA Le Rubis, Jarrie, France) identical to those used in a previous study (Castaing *et al.*, 1981), a coarse-grained (30–50 μm) polycrystalline ceramic (LUCALOX, General Electric), and a fine-grained (3–5 μm) ceramic made by SCT (Bazet, France). The major impurity in Verneuil grown sapphire is titanium (10 ppm). The polycrystalline ceramics contain MgO as a sintering aid and are likely contaminated by Na₂O, CaO and SiO₂. Hydrostatic annealing experiments and constant strain rate ($2 \times 10^{-5} \text{ s}^{-1}$) compression tests were performed using a solid salt confining medium, by methods used in an earlier study of alumina plasticity at $T < 1000^\circ\text{C}$ (Castaing *et al.*, 1981). The high pressure hydrothermal environment was obtained following techniques modified after those of Kronenberg *et al.* (1986). Specimens were sealed in gold capsules with gibbsite powder, which provided between 10

and 100 μl of water by decomposition above 550–600°C. The presence and character of hydrogen impurities were evaluated by measurements of infrared (IR) absorption bands due to OH stretching modes and results of wet mechanical tests were compared with those of experiments performed on dry single crystals and polycrystals.

IR absorption spectra

Seven small, sharp IR absorption bands due to OH stretching vibrations appear between 3308 and 3163 cm^{-1} for hydrothermally treated sapphire, with peak absorbances that are significantly larger than found for the starting material. These bands are strongly polarized and match those assigned to interstitial hydrogen defects which occur in association with titanium impurities. Semi-quantitative estimations of molar extinction coefficients for these defects suggest very small hydrogen concentrations ($\ll 1$ ppm or OH/10⁶ Al). Systematic increases in absorption bands with annealing time and temperature (Table 1) reveal that these hydrogen defects are introduced by diffusional transport from surfaces in contact with water.

We observe a much larger, broad IR absorption band at around 3400 cm^{-1} in sapphire deformed in the presence of water (Table 1) which is comparable to broad absorptions of hydrothermally grown sapphire (Mainprice *et al.*, 1993). This absorption is likely to represent OH stretching vibrations of molecular water (with concentrations of ~ 10 –40 ppm, averaged over sample dimensions) and we believe that its incorporation proceeds by alumina dissolution and deposition at crystal surfaces and interconnected microcracks. If so, precipitated alumina at surfaces and internal flaws may have concentrations comparable to those of hydrothermally grown sapphire (Table 1).

TABLE 1. Sapphire and aluminas examined by IR absorption after various treatments. Also shown a hydrothermally grown sapphire provided by D. Mainprice *et al.* (1993). Concentrations are in ppm or ppb (10⁻⁹) and in numbers of hydrogen atoms for 1 cm² of the specimens crossed by the IR beam. They are deduced from sharp lines and from broad bands

Run number Material types	Treatments	Type of spectra	Concentration	Number H/cm ²	Thickn mm
Starting sapph	See Castaing <i>et al.</i> , 1981	Sharp	45 ppb	10 ¹⁵	4.2
N796 sapphire	900°C, 167 h, p=1500 Mpa	Sharp	90 ppb	2 × 10 ¹⁵	4.2
N799 sapphire	1025°C, 41 h, p=1500 Mpa	Sharp	275 ppb	6 × 10 ¹⁵	4.2
N800 sapphire	900°C, 83 h ; 6.9% deformed at 700°C pressure = 1500 MPa; C-H present	Broad	36 ± 15 ppm	4 × 10 ¹⁶	
LUCALOX	Starting ; grain size 20–30µm	no broad	< 6 ppm	<4 × 10 ¹⁵	0.14
LUCALOX	900°C, 188 h, 1500 MPa ; 40µm grain;	Broad	10 ³ ppm	6 × 10 ¹⁷	0.12
LUCALOX	850°C, 44 h, ε≈30% at 850°C; 1500 MPa	Broad	1290ppm	10 ¹⁸	0.14
SCT	Starting ; grain size 3–5 µm	no broad	< 6 ppm	<2 × 10 ¹⁵	0.09
SCT N798	900°C, 188h, 1500Mpa	Broad	1690ppm	8 × 10 ¹⁷	0.1
Sapphire	Hydrothermal growth	Broad	750 ppm	7 × 10 ¹⁸	2

Sharp OH absorption bands are not observed for polycrystalline alumina specimens, before or after hydrothermal annealing, potentially due to increased scattering of IR radiation at grain boundaries and the smaller optical path lengths required for IR transmittance measurements, leading to higher detection limits. However, IR spectra of hydrothermally annealed and deformed ceramic specimens exhibit a large, broad OH absorption band at 3400 cm⁻¹ which is absent in spectra of the starting materials. Hydrogen concentrations of the hydrothermally annealed and deformed polycrystalline ceramics are estimated at 1000–1700 ppm (Table 1). However, C-H bands at 2900 cm⁻¹ are also present, which probably represent contamination of grain boundaries, presumably by epoxy and organics used in thin section preparation; thus, OH absorption measurements may include contributions from these impurities.

Mechanical properties

Stress-strain $\sigma\epsilon$ curves of sapphire single crystals and ceramic polycrystals are characteristic of plastic deformation, with a pronounced yield stress σ_Y appearing after an initial, elastic rise in σ . Even under dry conditions, sapphire can be deformed at high confining pressure at temperatures as low as 200°C (Castaing *et al.*, 1981). For alumina ceramics deformed under dry conditions, the Hall-Petch relation applies, with a friction stress equal to σ_Y for prism plane slip, which is an indication that dislocation glide dominates. In this study, we find that σ_Y of sapphire and alumina polycrystals are reduced significantly in the presence of water,

associated with the incorporation of hydrogen impurities. Sapphire deformed at 700–750°C exhibit σ_Y of 1400 MPa under dry conditions and 670 MPa in the presence of water. Coarse-grained LUCALOX and fine-grained SCT ceramics exhibit σ_Y of 2000 and 3000 MPa, respectively. The mechanisms of deformation at these stresses include dislocation motion and cracking. However, these ceramics deformed under hydrothermal conditions at σ_Y of 1040 and 470 MPa, respectively, and the predominant mechanisms of deformation are likely changed.

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