Structural Characterization of Natural Quartz by Scanning TEM

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For quartz, despite its industrial importance and an extensive amount of research done on it, there are still open fundamental questions, e.g. regarding crystal defects, phase changes or damage mechanisms under ionizing radiation [1,2]. Transmission electron microscopy (TEM), widely deployed to investigate crystal structures down to Å level, has scarcely been published with respect to quartz in the last decades. The reason for this, beside challenges in preparing good specimens, is that this mineral is very beam sensitive and rapidly becomes amorphous during TEM investigations.

Here, we present an assessment of modern field-emission gun (FEG) TEM (at 200 kV) for the study of high purity quartz. To get large areas to study and avoid radiation damage during preparation, bulk specimens of up to 3000 μm^2 of electron transparent material were prepared solely by mechanical wedge polishing. The specimens were selected from a petrographic thin section at specific positions and crystallographic orientations (Fig. 1(a)). Additionally, sand specimens were prepared by dispersing purified quartz grains (<12 µm) on a holey carbon TEM grid. Deteriorating specimen charging, common in the TEM, was avoided by either using sand specimens or scanning techniques.

It was found that the rate of amorphization is amongst others dependent on the amount of adjacent crystal to the illuminated volume. Scanning techniques with a fine probe size thus have a higher critical dose. For the scanning TEM (STEM) mode in a double corrected cold FEG JEOL ARM200F, a critical dose of 10.6 ± 2.6 [10^{24} e/m^2] was found for a probe size <0.8 Å, a 4 pA probe, a specimen thickness 80 nm and a [001] orientation. Dwell time was not found to have an influence on the damage rate. Both annular bright-field (ABF) and high-angle annular dark-field (HAADF) STEM lattice imaging (Fig. 1(b)) can be achieved. Using non-rigid registration on a series of very low dose ABF frames [3] as well as periodical and rotational averaging [4] it was possible for the first time to resolve single Si and O atom columns in beam sensitive quartz (Fig. 1(c)).

During TEM, beam damage can manifest itself as strain centers with an amorphous core, which were found to grow continuously, supporting previous findings [5,6]. Under repeated STEM exposure, these strain centers expanded (Fig. 2(a,b)). An alternative route to study quartz at low dose is by scanning precession electron diffraction (SPED) on a uncorrected Schottky FEG [7]. Several SPED scans could be applied without visually changing the specimen. Post-acquisition data analysis of the SPED data allows to visualize and analyze the strain around the centers (Fig. 2(c,d)). It was also possible to acquire SPED data on grain boundaries and dislocation networks. Furthermore, the low dose SPED method allowed to study the β- to α-quartz transition at 572.5°C using a DENS heating holder for the quartz sand. The whole grain changed phase instantaneously and no intermediate phase or twinning as previously been reported by [8,9] was observed. With continuous irradiation, the temperature of the β- to α-quartz was found to slightly decrease.

The conducted experiments show that a low dose approach with modern scanning FEG TEM can shed new light on phase transformations, crystallographic defects and damage mechanisms in quartz and encourage further low dose high-resolution TEM studies of beam sensitive minerals [10].

References:
[1] L.W. Hobbs, Nucl. Instr. Meth. in Phys. Res. **B 91** (1994) 30–42.
[2] B. Wang *et al*, J. Chem. Phys. **143** (2015) 024505 1–8.
[3] L. Jones *et al*, Adv. Struct. Chem. Imaging **1** (2015) 1–16.
[4] S. Wenner *et al*, Micron **96** (2017) 103–111.
[5] L.W. Hobbs, M.R. Pascucci, J. Phys. **41** (1980) 237–242.
[6] C.B. Carter, D.L. Kohlstedt, Phys. Chem. Miner. **7** (1981) 110–116.
[7] P.A. Midgley, A.S. Eggeman, IUCrJ **2** (2015) 126–136.
[8] G. van Tendeloo, J. van Landuyt, S. Amelinckx, Phys. Stat. Sol. **33** (1976) 723–735.
[9] P.J. Heaney, D.R. Veblen, Am. Mineral. **76** (1991) 1018–1032.
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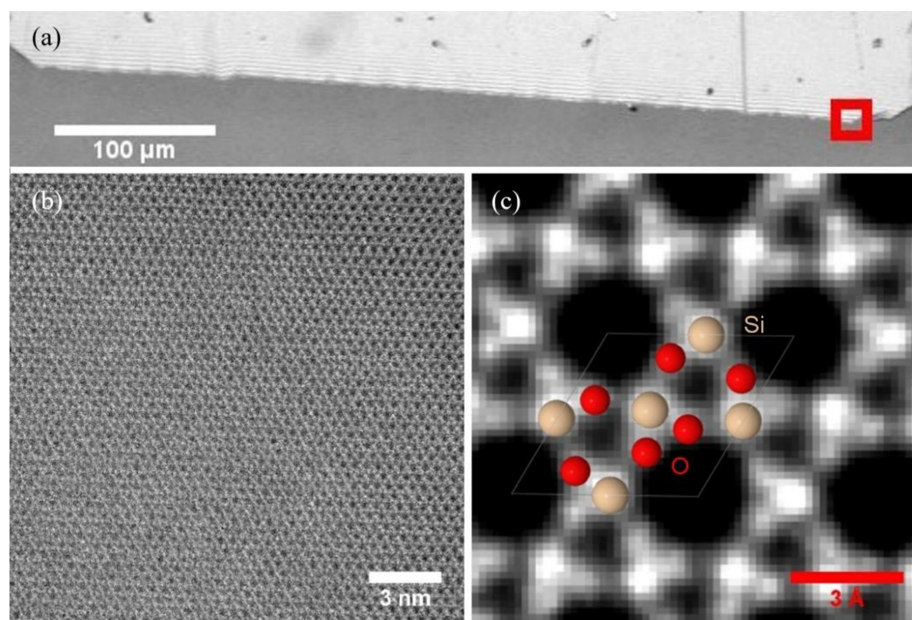

Figure 1. (a) Optical light microscope image of wedge polished bulk TEM specimen with [001] orientation. The area where (b) and (c) were acquired is marked by a red box. (b) Large area HAADF STEM lattice image. (c) Aligned, summed, periodically and rotationally averaged ABF STEM series (contrast inverted) with visible Si and O columns and unit cell model overlay.

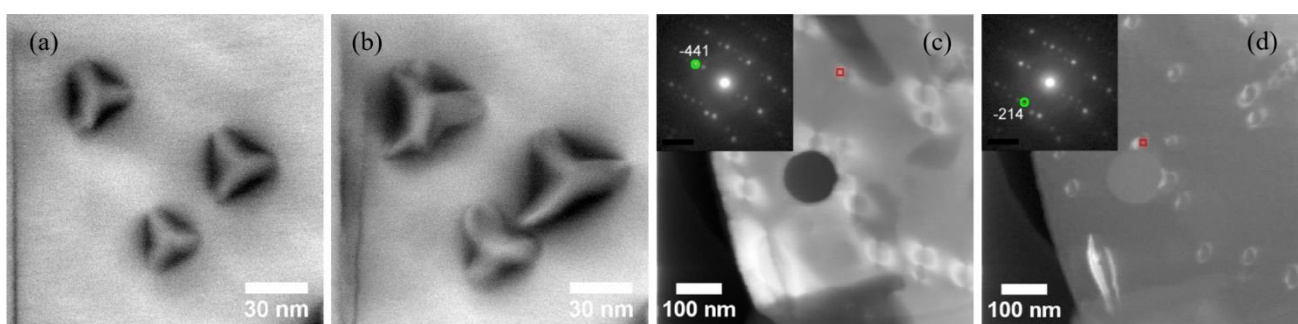

Figure 2. (a,b) BF STEM images of strain centers induced by TEM irradiation in a bulk specimen oriented on [001]. (a) Initial stage with strain contrast following the crystal symmetry. (b) After continued irradiation in STEM. The strain contrast area expanded and lost symmetry. (c,d) Virtual dark-field SPED images of a grain oriented on [551]. Inserts depict corresponding diffraction patterns from the point marked by a red square with the selected reflections for the virtual dark-field indexed and marked by a green circle. The central circular area is amorphous due to the SPED beam rest position.