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OH in enstatite and diopside at 6 GPa and 1150°C in the system $CaO-MgO-SiO_2-H_2O$

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Single crystals of diopside as well as enstatite were synthesized at 6 GPa and 1150°C under water-saturated conditions. The stoichiometry of chosen mixtures was corresponding to diopside plus small amounts of either forsterite+wollastonite, or wollastonite+coesite, or coesite+enstatite, or enstatite+forsterite. Crystals of diopside and enstatite were handpicked, embedded in thermoplastic resin for alignment parallel to (010) and (100) using a polarisation microscope, and studied by FTIR-spectroscopy in order to define the OH-incorporation mechanism.

Polarized IR spectra were recorded at room temperature in transmission mode. IR spectra of diopside exhibit two different OH-absorption bands at 3357 and 3598 cm^{-1}. The OH-absorption band at 3357 cm^{-1} is a prominent band and appears in all spectra and in each case shows the strongest absorption for $E||n_\gamma$. IR spectra of diopside, synthesized under lower silica activity (i.e. coexisting with Fo) exhibit an additional absorption band at 3598 cm^{-1}. This band is not presented in IR spectra of diopside coexisting with Coe and shows the strongest absorption for $E||n_\beta$. The probable explanation is that this absorption band appears because of lower availability of Si and is associated with tetrahedral OH-defects (T-site vacancies), while the band at 3357 cm^{-1} could be associated with octahedral defects (M-site vacancies). Spectra of diopside coexisting with coesite show the strongest absorption (i.e. the highest H_2O-content, reaching up to 160 ppm), while spectra of diopside from all other phase assemblages do not differ significantly in the integral absorbance and OH-content (reaching approximately 65 ppm).

From the assemblages Di+En+Coe and Di+En+Fo also enstatite crystals were studied by FTIR-spectroscopy. In addition to the OH-absorption bands of enstatite synthesized in the system $MgO-SiO_2-H_2O$ (i.e. at 3687, 3592, 3362 and 3067 cm^{-1}) IR spectra of enstatite coexisting with Di exhibit an absorption band at 3436 cm-1. This absorption band could be caused by generation of additional hydrous defects due to the incorporation of Ca that is incorporated up to 1.8 wt% in enstatite coexisting with diopside. The IR spectra of enstatite revealed a water concentration up to 220 ppm (wt) using the calibration of Libowitzky & Rossman (1997) and 450 ppm (wt) using the calibration of Stalder et al. (2012), respectively.