On hydrogen bonding of phase D: A Raman study

Masami Kanzaki[1]; Xianyu Xue[1]

[1] ISEI, Okayama Univ.

http://www.misasa.okayama-u.ac.jp/~masami/

We have recently studied local structure of phase D (dense hydrous magnesium silicate) by NMR spectroscopy. Contrary to previous single crystal XRD studies and Raman observations, ^{1}1H NMR revealed strong hydrogen bonding in phase D. In order to confirm the NMR result, micro-Raman study of OH stretching vibrations has been conducted, and is reported here (Xue et al., 2008).

We used both 488 and 513nm laser excitations to avoid bands due to fluorescence. Micro-Raman spectrometer, equiped with x50 objective lens, back scattering sampling, a 500mm spectrograph and LN2-cooled CCD detector, was used. The samples were synthesized at 24GPa, and 900 and 1100 C, by Dr. A. Shatskiy. It contains phase D with minor superhydrous B, as identified by NMR.

We idetified phase D and superhydrous B in the samples by micro-Raman, as expected. The Raman spectrum at lower wavenumber region of phase D was identical to those of previous reports (Ohtani et al., 1998; Frost and Fei, 1998). These previous studies have assigned single broad band at 2850cm^{-1} for phase D. However, we found three broad bands (2240, 2470, 2810cm^{-1}) which are attributable to phase D. The last band could be correspond to the band found in the previous studies. As these three bands are observed in both spectra taken using 488 and 514nm excitations, they are not due to fluorescence. We noted that a weak band at around 2470cm^{-1} can be also seen in the spectrum publishded by Frost and Fei (1998).

These three broad bands in 1800 - 3000 cm^{-1} region are well known feature for strong hydrogen bonding with O-H..O distance of about 2.55A (Novak, 1974). As for high-pressure phases, delta-AlOOH and phase egg which are known to have strong hydrogen bonding by XRD, NMR and Raman (e.g., Xue and Kanzaki, 2007), also show similar Raman bands. Therefore we concluded that phase D does have strong hydrogen bond, fully consistent with our ^{1}H NMR study.

References:

Frost, D.J. & Y. Fei (1998) JGR, 103, 7463.

Novak, A. (1974) in Structure and Bonding 18, 177-216, Springer.

Ohtani, E. et al. (1998) Min. J., 20, 163.

Xue, X. & M. Kanzaki (2007) J. Phys. Chem. B., 111, 13156, 2007.

Xue, X et al. (2008) Am. Mineral., in press.