High-temperature single crystal X-ray diffraction and FT-IR study of natural humite

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Crystal structures of a natural humite, $(Mg_{6.46}Fe_{0.49}Ti_{0.03}Mn_{0.02})_{7.00}Si_{3.00}O_{12}(F_{0.99}OH_{0.95}O_{0.06})_{2.00}$ from Tilley Foster mine in U.S.A. has been refined under high temperature conditions from 296 to 1023 K by single crystal X-ray diffractometer (RIGAKU, R-AXIS IV^{++}) equipped with rotating anode and a U-shaped resistence heater . The structure refinement were carried out using SHELEXL 97 (Sheldrick, 1997). The residual idexes (%) and GooF at 296K, 423 K, 573 K, 723 K, 873 K and 1023 K were 2.06 and 1.21, 2.85 and 1.20, 2.90 and 1.20, 2.55 and 1.15, 2.78 ans 1.20 and 3.37 and 1.16, respectively. FT-IR spectra of natural humite was observed under high temperature conditions from 296 to 1323 K.

As results from high temperature X-ray diffraction analyses, the thermal expansion coefficients of lattice constants and volume of humite up to 873 K are as follows, a_a=9.4(3), a_b=12.9(2), a_c =11.9(3), and a_V=33.5(4) (x10^{-6}K^{-1}). The thermal expansion coefficient of the direction perpendicular to the closest packing oxygen layer is the smallest.The thermal expansions of *c*-axis direction of humite was discontinuous around 1023K.Structure refinements of humite showed the changing trends of all distances and angles related to the OH/F in M3 site changed at 1023K. Especially, the negative change of M3-M3 distances at 1023K of both samples would affected the change of *c*-axis. In contrast, OH/F...OH/F distance increases smoothly up to 1023K.

In the FT-IR spectra observation of natural humite, three OH stretching vibrational peaks were observed at 3567, 3558, 3385cm^{-1} under ambient condition.Peaks at 3567, 3558cm^{-1} slightly shifted to lower wavenumber. Peak at 3385 cm^{-1} shifted to higher wavenumber. The positive shift of this peak suggested that the effects of hydrogen bonding would be weaken under high temperature conditions. These observations implied that the stability of humite and chondrodite would be related to the decline of O/F...H hydrogen bonding.