INTRODUCTION

The most significant work on the crystal chemistry of humites occurred over a ten-year period beginning about 1968. Initial studies focussed primarily on the chemistry and crystallographic nomenclature (Ribbe et al. 1968; Jones et al. 1969; Jones 1969). This was followed by a series of single-crystal X-ray refinements of the structures of norbergite (Gibbs and Ribbe 1969), chondrodite (Gibbs et al. 1970), humite (Ribbe and Gibbs 1971), clinohumite and titanian clinohumite (Robinson et al. 1973; Kocman and Rucklidge 1973; Fujino and Takéuchi 1978), and OH-chondrodite (Yamamoto 1977). More recently, single-crystal X-ray refinements have been reported for norbergite (Cámara 1997) and a natural hydroxylclinohumite (Ferraris et al. 2000). The crystal structure of titanian clinohumite has also been refined using single-crystal neutron diffraction data (Smyth et al. 1994).

The humites can be represented by the general formula, $n[Mg_2SiO_4]·[M_1−xTi_x(\text{F,OH})_2−2xO_2]$, where $M$ is primarily Mg with minor amounts of Fe$^{2+}$, Mn, Ni, Ca, Zn, Cu, $0 \leq x \leq 0.5$ and $n = 1, 2, 3, 4$ for norbergite, chondrodite, humite, and clinohumite, respectively. The $[O, (OH,F)]$ atoms are arranged in hexagonal closest packed arrays with $M$ and Si cations occupying the octahedral (50%) and tetrahedral (8–12%) for $n = 1–4$ sites (Ribbe 1980). The $(\text{F,OH,O})$ anion is triangularly coordinated to three $M$ cations. In terms of a polyhedral model, the structures consist of chains of edge-sharing octahedra linked by silicate tetrahedra. The positions of the $H$ atoms have been determined for OH-chondrodite (Yamamoto 1977), titanian clinohumite (Fujino and Takéuchi 1978; Smyth et al. 1994), norbergite (Cámara 1997), and hydroxyc clinohumite (Ferraris et al. 2000). Structure-energy calculations have also been used to locate H-atom positions in several humite minerals, including OH-chondrodite and titanian clinohumite (Abbott et al. 1989).

Experimental work in the MgO-SiO$_2$-H$_2$O (MSH) system has shown that both OH-clinohumite and OH-chondrodite are stable at $P-T$ conditions (700–1100 °C and 2.9–7.7 GPa) representative of the upper mantle (Yamamoto and Akimoto 1977; Akaogi and Akimoto 1980). More recent investigations in both the MSH system, and natural or synthetic systems that mimic the composition of typical mantle rock, have extended the stability range of both OH end-members to approximately 14 GPa at 1100 °C (Khodyrev et al. 1992; Kawamoto et al. 1995; Luth 1995; Burnley and Navrotsky 1996; Wunder 1998).

In recent years, there has been a resurgence of interest in chondrodite and clinohumite among spectroscopists who have investigated elastic properties (Beckman Fritzel and Bass 1997; Sinogeikin and Bass 1999) and the pressure and/or temperature dependence of OH vibrational frequencies (Williams 1992; Lin et al. 1999; Hofmeister et al. 1999; Mernagh et al. 1999; Lin et al. 2000). Spectroscopic methods have also been used to probe the nature of the H-atom environment in both natural F-bearing chondrodite and synthetic OH-chondrodite and OH-clinohumite (Akaogi and Akimoto 1986; Cynn et al. 1996; Phillips et al. 1997). Bulk moduli determined from diffraction data have been reported for F-bearing chondrodite (Faust and Knittle 1994; Kuribayashi et al. 1998; Friedrich et al. 2000).

O-D⋯O bond geometry in OD-chondrodite

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ABSTRACT

The crystal structure of OD-chondrodite [Mg$_5$Si$_2$O$_8$(OD)$_2$, $P2_1/b$ (a unique), $a = 4.74711(5)$, $b = 10.34888(16)$, $c = 7.90228(13)$ Å, $\alpha = 108.678(1)^\circ$] was refined to $wR_p = 0.0218$, $\chi^2 = 3.545$ at ambient conditions using time-of-flight neutron powder data. The disordered H model proposed for OH-chondrodite on the basis of single-crystal X-ray data is confirmed. The occupations of the D1 and D2 sites are, respectively, 0.52(1) and 0.48(1). The long O5-D1 [1.076(4) Å] and O5-D2 [1.111(4) Å] bond lengths, which are two of the longest O-H(D) bonds observed in mineral structures, reflect the positional disorder of the O5 atom in the unshared OH-OH edge. Both D1 [1.968(4), 2.489(4) Å] and D2 [2.149(4), 2.251(4) Å] atoms are involved in two hydrogen bonds. A re-examination of the origin of positive OH frequency shifts in both F-bearing and OH-chondrodite at high pressure is warranted in view of the crystallographic data.