

LETTERS

First synthesis of the hydroxyl end-member of humite, $\text{Mg}_7\text{Si}_3\text{O}_{12}(\text{OH})_2$

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ABSTRACT

The hydroxyl end-member of humite, $\text{Mg}_7\text{Si}_3\text{O}_{12}(\text{OH})_2$, was synthesized at 30 kbar and 940 °C in the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$ (MSH). Optical properties are $n_x = 1.6348(10)$, $n_y = 1.6397(10)$, $n_z = 1.6612(10)$, $2V_z = 56.1(2)^\circ$, $-\Delta_n = 0.026$. Results of single-crystal X-ray diffraction gave $a = 4.78(2)$, $b = 10.22(3)$, $c = 21.02(9)$ Å, $V = 1027(7)$ Å³, space group = *Pbnm*. The morphology of the synthetic humite crystal is comparable to that of natural F-rich humite. Microprobe analyses confirmed a nearly ideal formula, $\text{Mg}_{6.97(3)}\text{Si}_{3.02(1)}\text{O}_{12}(\text{OH})_{2.00(2)}$.

INTRODUCTION

The general chemical formula of humite group minerals is $\text{M}(\text{OH},\text{F})_2 \times n\text{M}_2\text{SiO}_4$, where $\text{M} = \text{Mg}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Ti}$, etc., and $n = 1$ for norbergite, $n = 2$ for chondrodite, $n = 3$ for humite, and $n = 4$ for clinohumite. Minerals of this series occur in metamorphosed and metasomatic limestones and dolomites. Additionally, Mn-rich humite has been found in skarns (Moore, 1978), and Ti-rich chondrodite and clinohumite have been found in kimberlitic xenoliths (e.g., McGetchin et al., 1970; Aoki et al., 1976). With the exception of the Mn- and Ti-rich phases, which are nearly F-free, the humite group phases contain both OH and F. For example, the humite-group phases from limestones have the following (OH)/(OH + F) values: 0.19–0.30 norbergite, 0.22–0.37 chondrodite, 0.38–0.51 humite, and 0.47–0.54 clinohumite (Rankama, 1938; Sahama, 1953; Jones, 1968). The replacement of OH by F seems to decrease in the series from norbergite to clinohumite.

In the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$ (MSH, Fig. 1), until now only synthetic OH end-members of chondrodite (phase D, Yamamoto and Akimoto, 1974) and of clinohumite (Yamamoto and Akimoto, 1977) have been known. Both were synthesized in the *P-T*-range 29–77 kbar, ~700–1000 °C, and are possible containers of H_2O in the Earth's upper mantle (e.g., Thompson, 1992).

Here we report the synthesis and some properties of the OH phase with $n = 3$, $\text{Mg}_7\text{Si}_3\text{O}_{12}(\text{OH})_2$. As in the case of the synthetic hydroxyl end-member of the topaz series (Wunder et al., 1993), we informally call this phase "humite-OH," and the known monoclinic hydroxyl end-members are labeled "chondrodite-OH" and "clinohumite-OH" in Figure 1.

SYNTHESIS

The successful high-pressure experiment was performed in a piston-cylinder press constructed after Boyd and England (1960). The pressure cell consisted of rock salt, fired pyrophyllite, and a carbon cylinder as a resistance furnace. The 2σ uncertainty in *P* is about 1%; temperature was monitored using a chromel-alumel thermocouple with an accuracy of about 10 K.

Conditions of synthesis were 30 kbar, 940 °C, and 24 h using a mixture of phases to determine the equilibrium reaction chondrodite = clinohumite + brucite (see Fig. 1). The three phases were previously synthesized as pure phases in the MSH-system and then mixed in the Mg/Si-proportions of chondrodite. About 10 mg of the solid material plus 20 wt% of water were filled into an Au-tube of 8 mm length. After the experiment, independent of the products of the equilibrium experiment, a few relatively large crystals of an unknown phase were observed in the upper part of the Au tube. For further characterization, one single crystal of $100 \times 100 \times 40$ μm (Fig. 2) was selected and mounted on a glass fiber.

MORPHOLOGY AND OPTICS

The crystal forms short orthorhombic bipyramids (Fig. 2). This morphology is typical of natural F-rich humite (Tröger, 1982).

The optical data of the single crystal selected were measured using a microrefractometer spindle stage as described by Medenbach (1985), which also allows the precise determination of $2V$ by direct conoscopic investigation. The data (Table 1) are, in principle, similar to those known for all natural humite group phases (e.g.,

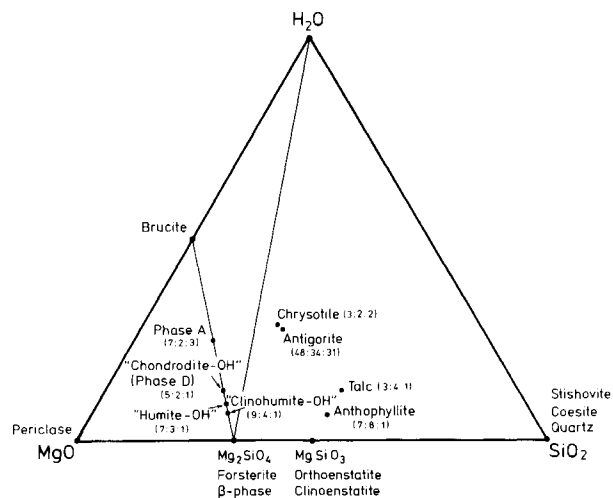


Fig. 1. Selected phases of the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$ (MSH) synthesized at pressures below 100 kbar. The molar ratios of $\text{MgO:SiO}_2\text{:H}_2\text{O}$ are given in parentheses.

Deer et al., 1992). However, significant differences were noted when the optical data of the new phase were compared with those given by Yamamoto and Akimoto (1974) for chondrodite and by Yamamoto and Akimoto (1977) for clinohumite (Table 1). Additionally, the new phase shows straight extinction, thus distinguishing it from the monoclinic OH end-member homologues. Because the mean refractive index \bar{n} of the new phase is close to the value of a theoretical OH humite end-member as calculated by Sahama (1953), and because this value lies nearly midway between those of the OH end-members of chondrodite and clinohumite (Table 1), it seems likely the unknown phase is the OH end-member of humite.

X-RAY DATA

Single-crystal photographs of the crystal shown in Figure 2 were taken on a STOE precession camera using Zr-filtered $\text{MoK}\alpha$ radiation. The crystal was first oriented with regard to its morphology using the spindle stage. Photographs taken from the $0kl$, $1kl$, $hk0$, and $hk1$ layers did not show any reflections that violate the orthorhombic space group $Pbnm$, which was chosen because of the structural relation of humite to forsterite (Jones, 1969). The values of d correspond closely to those given on JCPDS card no. 12-755 for natural humite. Two cone-axis photographs gave 4.75 and 20.92 Å, which correspond to the known values of a_0 and c_0 of natural humite.

Subsequently, the crystal was investigated on a four-circle single-crystal diffractometer (SIEMENS P3). An orthorhombic unit cell was found with $a = 4.78(2)$, $b = 10.22(3)$, $c = 21.02(9)$ Å, and $V = 1027(7)$ Å³. The relatively high standard deviation is the result of the poor quality of the crystal which yielded split reflections.

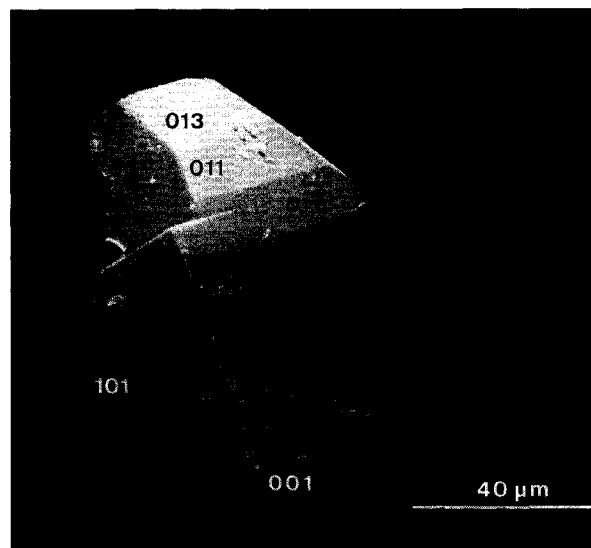


Fig. 2. Scanning electron micrograph showing the morphology of synthetic humite. Indexing of the faces according to Tröger (1982).

CHEMICAL COMPOSITION

The chemical composition of the crystal shown in Figure 2 was determined by a CAMECA SX 50 electron microprobe at Ruhr University Bochum. Synthetic pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) served as a standard.

The average of nine individual analyses gave (in weight percent) MgO 58.48(0.21), SiO_2 37.77(0.16), and H_2O (determined by difference) 3.75(0.28). On the basis of 14 atoms and with the assumption that H_2O is present in the form of OH groups, the structural formula $\text{Mg}_{6.97(3)}\text{Si}_{3.02(1)}\text{O}_{12}(\text{OH})_{2.00(2)}$ was calculated. Within the precision of measurements this corresponds nearly perfectly to the formula of the OH end-member of humite, $\text{Mg}_7\text{Si}_3\text{O}_{12}(\text{OH})_2$.

To assess the compatibility of the optical data, the X-ray density ($\rho_r = 3.106 \text{ g/cm}^3$), and the chemical formula, the Gladstone-Dale relationship was tested. The $Kp/Kc-1$ parameter was calculated as 0.001, which indicates an ideal consistency (the "superior" category of Mandarino, 1979).

TABLE 1. Optical data of the OH end-members of humite, chondrodite, and clinohumite

	Chondrodite (Yamamoto and Akimoto, 1974)	Humite (this work)	Clinohumite (Yamamoto and Akimoto, 1977)
n_x	1.630(2)	1.6348(10)	1.638(2)
n_y	1.642(2)	1.6397(10)	1.641(2)
n_z	1.658(1)	1.6612(10)	1.669(1)
\bar{n}	1.643	1.645	1.649
$-\Delta n$	0.028	0.026	0.031
$2V_x$ (°)	?	56.1(2)	?

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