Ca$_3$SiO$_3$OHF—A high-pressure phase with dense calcium polyhedral packing and tetrahedral silicon

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ABSTRACT

The composition and structure of a new phase crystallizing in high-pressure experiments in the system CaO-Ca(OH)$_2$-CaF$_2$-SiO$_2$ are described. The composition is on the join Ca$_3$SiO$_3$(OH)F$_2$-Ca$_3$SiO$_3$F$_2$, with the relative amounts of OH and F near 50/50 from electron probe microanalysis, or near the ideal midpoint composition Ca$_2$SiO$_3$OHF. The symmetry is monoclinic, space group $P2_1/c$, with $a = 5.8111(7)$, $b = 10.6050(13)$, and $c = 6.6968(8)$ Å, and $\beta = 102.025(3)^\circ$, $V = 403.65(8)$ Å$^3$, $Z = 4$. In the structure isolated SiO$_3$OH tetrahedral groups occupy narrow linear channels whose axes lie along a. The channels are lined by two types of eight-coordinated CaO$_5$OHF$_2$ polyhedra that share edges and faces. The axes of the channels lie on a nearly hexagonal array in the b-c plane, leading to a $c/b$ ratio of 0.618, close to the ideal ratio of 0.577 for a hexagonal array. However, there is no simple packing rule for either the cation or anion array. Although the channels are arranged in a nearly hexagonal fashion, the overall symmetry of the structure is not hexagonal, but instead has 5-rings of calcium polyhedra around the channels. The calcium atoms lie on a 5-3-5-3 net of triangles and pentagons that can be compared to the $\alpha$-UO$_3$ net.

INTRODUCTION

The calcium silicates exhibit complex structural behavior, with a variety of structures occurring at ambient and high pressures in the compositions Ca$_3$SiO$_5$, Ca$_2$SiO$_4$, Ca$_3$Si$_2$O$_7$, and CaSiO$_3$. The tendency for unusual structural behavior in these compounds is well documented. One example is CaSiO$_3$ perovskite, a high-pressure phase that spontaneously converts to an amorphous phase while pressure is being released (Ringwood and Major 1971). A second example is high-pressure Ca$_3$SiO$_4$ titanite, which develops five-coordinated silicon during pressure release under nonhydrostatic stress, the first documented example of this arrangement in a crystalline solid (Angel et al. 1996; Angel 1997; Stebbins and Poe 1999).

The addition of monovalent anions such as OH$^-$ and F$^-$ to the calcium silicate system allows additional structural flexibility. The system CaO-SiO$_2$-H$_2$O, for example, has silicate compounds with at least 25 distinct compositions (from the ICSD database; cf. Fluck 1996) stable at ambient pressure. Many new phases were also uncovered in an exploratory study of the system CaO-SiO$_2$-CaCl$_2$ by Stade at al. (1998). The monovalent anions significantly change the structural behavior of silicates because they have lower coordination and/or weaker bonds to metals, requiring only half as much total bond valence in order to be saturated. This modifies the structural networks, reducing the polymerization of the structure, and leaving voids, channels, etc. At the same time, the coordination numbers of the cations tend to increase when monovalent anions are added to a silicate, simply because there are more anions present in the structure. Given the interesting structures found in the CaO-SiO$_2$ system, new structural behavior can be anticipated when monovalent anions are added to this system and pressure is used as a variable. For example, new examples of pentacoordinate silicon could potentially be found in this system, as they are in the silica zeolites grown with fluorine, which form SiO$_4$F polyhedra (Koller et al. 1999).

Among the many already known examples of mixed-anion phases containing calcium and silicon and occurring at ambient pressure are structures such as cuspidine [Ca$_3$Si$_2$O$_4$(OH)$_2$F] (Saburi et al. 1977), and various cement minerals such as $\alpha$ and $\beta$-Ca$_3$Si$_2$O$_6$(OH)$_2$ (Yano et al. 1993; Marsh 1994; Dai and Post 1995; Xu and Buseck 1996). The majority of these, because of their low structural density, are not likely high-pressure phases. In order to shed light on the effect of pressure on these compositions, high-pressure structural studies in the system Ca-Si-O-OH-F are being pursued. Exploratory work in the Ca$_2$SiO$_3$F$_2$-Ca(OH)$_2$ system has resulted in the growth of crystals with compositions near Ca$_3$SiO$_3$OHF.

EXPERIMENTAL METHODS

The unknown compound was encountered during a series of experiments on compositions containing Ca(OH)$_2$, CaF$_2$, and SiO$_2$ in various proportions and at various pressures and temperatures. A list of the pertinent high-pressure experiments is shown in Table 1. Reagent grade CaF$_2$ (Fisher) and SiO$_2$ (SPIEX Industries, Inc.) were used as purchased. In order to avoid the common problem of contamination by CO$_2$, fresh batches of Ca(OH)$_2$ were made by treating CaO (made by calcining CaCO$_3$ (Baker) at 960 °C and quenching in the absence of CO$_2$) in boiling water. This technique has been found in the past by Raman spectroscopic analysis, which is very sensitive to the presence of CO$_2$ groups, to result in samples of Ca(OH)$_2$, with no detectible CaCO$_3$ impurity. The starting materials were mixed by grinding under ethanol in an agate mortar and pestle.

For each high-pressure experiment, about 25 mg of starting material was placed in a platinum capsule 3.5 mm in diameter and 0.13 mm thick, and the capsule was welded at both ends using “trash can lids” made from 0.13 mm platinum foil (Holloway et al. 1992). The pressure, thermocouple temperature, and duration

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