Structural variation in the ferrobustamite solid solution

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Abstract

Ferrobustamite, WO₃₆F₃₁, from the Ofuku mine, Yamaguchi Prefecture, Japan, is close to the Fe-poor end of the ferrobustamite solid solution. Its crystal data are: space group $AT_1$, $a = 7.862$, $b = 7.253$, $c = 13.967$ Å, $\alpha = 89^\circ44'$, $\beta = 95^\circ28'$, $\gamma = 103^\circ29'$, and $12[Ca_{0.65}Fe_{0.15}Mn_{0.2}SiO_2]$ in the unit cell. Our refinement of its structure reveals that it possesses pseudo-mirrors which are more nearly true mirror planes than those in the WO₃₆F₃₀ structure, and the small size of one cation site, $M_3$, in the structure induces the concentration of the Fe(Mn) content into it, thus giving the solid solution the Fe-poor limit of WO₃₂₅F₁₆₇. The Mössbauer spectra of the specimen showed that, after a heat treatment at 1,140°C, the degree of concentration of Fe at $M_3$ decreases, suggesting that the site occupancies of Fe atoms vary with the temperature of formation and the cooling process of the crystal.

Introduction

Bowen et al. (1933) presented a phase diagram of the system CaO-FeO-SiO₂ showing an extensive solid solution at temperatures above 1,000°C, and called it the “wollastonite solid solution.” Tilley (1937) first described a mineral with a composition of 77 mole percent CaSiO₃ and 23 percent FeSiO₃ (WO_{37}F_{52}) from Scafell Hill, County, Antrim, and named it “iron-wollastonite.” He further reported another iron-wollastonite from contact skarns at Skye, Scotland (Tilley, 1948).

A reexamination by Rutstein (1971) of the CaSiO₃-CaFeSiO₃ system showed that there are two different phases in this system, and these are compositionally separated from each other by a gap extending from WO{sub 36}F{sub 31} to WO{sub 37}F{sub 52}. Rutstein and White (1971) analyzed infrared spectra of these samples, and suggested that those rich in iron have a structure analogous to that of bustamite.

The crystal structures of two pyroxenoids, a synthetic phase, Ca₀.₆₂Fe₀.₇₅SiO₃ (WO₃₆F₃₀), and a natural phase, Ca₀.₆₂Fe₀.₇₅Mn₀.₀₂SiO₃ (WO₃₇F₃₁), both refined by Rapoport and Burnham (1973), are similar to each other and to that of bustamite. This species was therefore named ferrobustamite by these authors, who pointed out that the Fe-poor end-member of this phase region is expected on structural grounds to lie at WO₃₂₅F₁₆₇.

Shimazaki and Yamanaka (1973) discovered a miscibility gap between wollastonite and ferrobustamite, and suggested that ferrobustamite with an Fe content larger than that of Ca₀.₆₂Fe₀.₇₅SiO₃ (WO₃₇F₃₁) will be stable at the low temperatures appropriate for skarn formation, probably 300–600°C. Matsueda (1973, 1974) also reconfirmed that ferrobustamite is distinct from wollastonite in optical and chemical properties and cell dimensions, and considered paragenetic relations between ferrobustamite and wollastonite. Compositional limits of wollastonite, bustamite, and ferrobustamite were also discussed by Mason (1975).

Since the structure refinement of the natural phase, WO₃₂₅F₁₆₇, reported by Rapoport and Burnham (1973), was hindered by the twinned crystal used for the structure determination, we consider it necessary to reexamine the structure with a well-specified crystal. Also the structure of ferrobustamite in the Fe-poor limit was of particular importance for clarifying structure variations of the solid solution. We have therefore undertaken a structural investigation of Ca₀.₆₁Fe₀.₁₅Mn₀.₀₆SiO₃ and compared our results with the data previously obtained from other members of the series.

Refinement of the ferrobustamite structure

The crystal used in the present investigation was found in the Ofuku mine, Yamaguchi Prefecture,