A refinement of the crystal structure of ohmilitite, 
Sr₃(Ti,Fe³⁺)(O,OH)(Si₂O₆)₂・2−3H₂O

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Abstract

The monoclinic unit cell of ohmilitite, Sr₃(Ti,Fe³⁺)(O,OH)(Si₂O₆)₂・2−3H₂O, has dimensions a = 10.979(6), b = 7.799(5), c = 7.818(4)Å, β = 100.90 (3)°, and space group P2₁/m; Z = 2, V = 657.4(6)Å³. The crystal structure has been refined to an R-value of 5.9% for 2121 independent reflections. Vertex-sharing Ti–O octahedra form chains parallel to b. Each of the octahedral chains is flanked by a pair of [Si₂O₆] chains, which are similar to those found in batiste and haradaite, thus forming a composite chain of composition [Si₂O₆][(Ti₂O₈)Si₂O₆]²⁻. These composite chains are joined together by Sr atoms and water molecules to form the structure. Of the three independent Sr atoms, Sr(1) and Sr(3) are 3-coordinated, with average Sr–O distances of 2.675Å. Sr(2) is 8-coordinated, with average bond length of 2.586Å. The average Ti(Fe)–O bond length is 1.992Å. Average Si–O distances are 1.643 and 1.606Å for bridging and nonbridging bonds, respectively. As consistent with the IR data, hydrogen is present as both H₂O and OH. The former forms hydrogen bonds with the oxygen atoms of the composite chains, with O–O distances from 2.69 to 2.83Å. The latter is associated with the octahedral cations in accordance with the substitution scheme, Ti²⁺O²⁻ → Fe³⁺OH⁻.

Introduction

Ohmilitite, Sr₃(Ti,Fe³⁺)(O,OH)(Si₂O₆)₂・2−3H₂O, was found in riebeckite-albite units in serpentinites from Ohmi, Niigata Prefecture, Central Japan and was described as a new mineral by Komatsu et al. (1973). It occurs as spherulites composed of radially arranged fine needles or fiber-like crystals which are generally less than 10 μm in diameter. The chemical analysis (Komatsu et al., 1973) gave SiO₂ 34.79, TiO₂ 10.27, Fe₂O₃ 0.20, SrO 47.37, H₂O 6.68 with a total of 99.31 weight percent. The chemical formula Sr₃Ti₃Si₄O₁₂(OH)•2H₂O was proposed assuming that titanium is trivalent. However, according to a suggestion made by Dr. A. Kato the formula has been revised to Sr₃Ti₂[O₃Si₂O₁₆]•2H₂O or Sr₃(Ti,Fe³⁺) [(O,OH)]Si₂O₆]•2H₂O such that the titanium is present as Ti²⁺.

The crystal structure of ohmilitite has been determined and refined to an R-value of 14% (Mizota et al., 1973), showing that ohmilitite has a chain structure similar to that of haradaite (Takeuchi and Joswig, 1967). The relatively high value of the R-factor was due to the poor quality of the crystal used. Because we have recently found a crystal fragment of high quality, we have undertaken the refinement of the crystal structure. The present paper describes the detailed structure of ohmilitite and discusses the configuration of the silicate chains and the role of the hydrogen atoms in conjunction with data from infrared absorption spectrometry and DSC-TG.

Experimental

X-ray diffraction

A crystal fragment having dimensions of approximately 0.6 × 0.1 × 0.04 mm was used for the present study. Unit cell dimensions were determined utilizing a Philips PW1100 single-crystal diffractometer using graphite-monochromated MoKα radiation (λ = 0.71069Å). The cell dimensions, obtained by least-squares refinement with 25 independent reflections, are a = 10.979(6), b = 7.799(5), c = 7.818(4)Å, β = 100.90(3)°, V = 657.4(6)Å³.