Cafetite, Ca[Ti₂O₅](H₂O): Crystal structure and revision of chemical formula

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ABSTRACT

The crystal structure of cafetite, ideally Ca[Ti₂O₅](H₂O), (monoclinic, P2₁/n, a = 4.9436(15), b = 12.109(4), c = 15.911(5) Å, β = 98.937(5)°, V = 940.9(5) Å³, Z = 8) has been solved by direct methods and refined to R₁ = 0.057 using X-ray diffraction data collected from a crystal pseudo-merohedrally twinned on (001). There are four symmetrically independent Ti cations; each is octahedrally coordinated by six O atoms. The coordination polyhedra around the Ti cations are strongly distorted with individual Ti-O bond lengths ranging from 1.743 to 2.223 Å (the average <Ti-O> bond length is 1.98 Å). Two symmetrically independent Ca cations are coordinated by six and eight anions for Ca₁ and Ca₂, respectively. The structure is based on [Ti₂O₅] sheets of TiO₆ octahedra parallel to (001). The Ca atoms and H₂O groups are located between the sheets and link them into a three-dimensional structure. The structural formula of cafetite confirmed by electron microprobe analysis is Ca[Ti₂O₅](H₂O), in contrast to the formula (Ca,Mg)(Fe,Al)₂Ti₄O₁₂·4H₂O suggested by Kukharenko et al. (1959). The wrong chemical formula suggested for cafetite by Kukharenko et al. (1959) is probably due to admixtures of magnetite or titanomagnetite in their samples. Cafetite is chemically related to kassite, Ca₂[Ti₂O₅](OH)₂, but differs from it in structure and structural formula.

INTRODUCTION

Cafetite was first described by Kukharenko et al. (1959) from alkaline rocks in the Afrikanda massif, Kola peninsula, Russia. The mineral was found in close association with titanomagnetite, phlogopite, ilmenite, baddeleite, chlorite, titanite, and an “undefined” mineral later described by Kukharenko et al. (1965) as kassite. As pointed out by Kovyazina gave the empirical formula (Ca0.67 Na0.06 K0.05 Fe0.18 Mg0.02 Mn0.02 Al0.12 Ti1.92 O4·H2O). The mineral was reported as orthorhombic, a = 12.10(2), b = 9.55(3), c = 4.95(1) Å, V = 1884.01 Å³. However, optical studies indicated that the γ axis of the optical indicatrix and the c axis are inclined to each other by ~2–4°, which suggested that cafetite is monoclinic.

Later, Kukharenko et al. (1965) provided a full description of the “undefined” mineral which they named kassite. Its ideal chemical composition was CaTi₂O₄(OH)₂, i.e., identical to that of kassite as described by Kukharenko et al. (1965). As a consequence, Evans et al. (1986) suggested that samples of cafetite and kassite were somehow intermixed by Kukharenko et al. (1959, 1965) during their X-ray study. As a consequence of Evans et al. (1986), the cafetite and kassite entries were interchanged in Set 39 of the powder diffraction file (PDF-2) (see also Self and Buseck 1991). For the mineral they designated as kassite, Evans et al. (1986) reported an orthorhombic cell, a = 12.10(2), b = 31.65(3), c = 4.95(1) Å, V = 1899 Å³, with possible space groups Ammma, A222, or A222.

Self and Buseck (1991) described kassite from Josephine Creek, Oregon, and studied the structure using electron-diffraction techniques. They found a B-centered orthorhombic unit cell with dimensions a = 9.08, b = 4.78, c = 5.23 Å, which is similar to that determined by Kukharenko et al. (1965) for kassite, except that the b dimension is halved. Chemical analyses showed that the chemical formula of the mineral under study was essentially Ca₂Ti₂O₄(OH)₂, i.e., identical to that of kassite. On the basis of their studies, Self and Buseck (1991) suggested a structure model for kassite that is similar to that of lucasite-Ce, Ce₂Ti₂O₄(OH)₂ (Nickel et al. 1987). Comparing their results with those of Evans et al. (1986), Self and Buseck (1991) pointed out that “…kassite and cafetite should not be distinguished by Fe content but rather by crystallographic properties” and that “…the status of kassite and the related mineral cafetite are destined to remain controversial until more specimens have been characterized.”

Recently, Yakovenchuk et al. (1999) found cafetite in two...