The crystal chemistry of welshite, a non-centrosymmetric (P1) aenigmatite-sapphirine-surinamite group mineral

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ABSTRACT

Previous attempts to refine the crystal structure of welshite, known only from Långban, Sweden, have been foiled by its extensive polysynthetic twinning, and without a structure determination, derivation of a reasonable formula has been difficult due its eclectic chemical composition. We report a successful refinement [wR(F2) = 0.0566 for 8048 unique reflections] in the non-centrosymmetric space group P1 of a relatively little twinned crystal (4% chiral) from sample NRM040068: a = 10.394(3) Å, b = 10.777(3) Å, c = 8.896(2) Å, α = 105.953(4)°, β = 96.294(4)°, γ = 124.948(3)°, V = 738.8(3) Å3, Z = 1. The refined formula, Ca3.78Mg7.87Sb3.00Mn1.35Si5.73Be3.33Al1.71Fe3+0.95O36, is in reasonable agreement with a formula determined by electron microprobe and Mössbauer spectroscopy (Be from the refinement), Ca3.81Mg7.84Sb3.03Mn1.17Zn0.04Fe2+0.45O36. The P1 symmetry of welshite 040068 is mainly a result of its cation distribution, which is driven by charge ordering on both the octahedral and tetrahedral sites as supported by calculation of electrostatic site potentials. Welshite can accommodate up to 3.46 Be per 40 O atoms by including several T sites with 100% Be occupancies without the formation of unfavorable tetrahedral Be-O-Be linkages that would result in the related centrosymmetric structures of sapphirine, khmaralite, makarochkinite, and høgtuvaite, none of which contain >2.1 Be per 40 O. A generalized formula for welshite is (Ca,Mn)0.054(Si,As)6(Be,Al)4(Al,Fe3+)2O36. Compositions of most of the samples, including NRM040068, can be expressed in terms of two idealized Al and Fe end-members Ca4Mg8Fe2+O4[Si6Be3Al3O36] and Ca3.81Mg7.84Sb3.03Mn1.17Zn0.04Fe2+0.45O36, respectively; the latter is the most representative for welshite and could be used in databases.

Keywords: Welshite, beryllium, antimony, crystal structure, charge ordering, Mössbauer spectroscopy, electron microprobe, ion microprobe

INTRODUCTION

Welshite is one of six minerals in the aenigmatite-sapphirine-surinamite group (Strunz and Nickel 2001) to contain significant amounts of Be. We have chosen the more inclusive grouping of Strunz and Nickel (2001) because it emphasizes the close relationship of the Be-bearing minerals surinamite and sapphirine-khmaralite to makarochkinite and høgtuvaite, which are two Be minerals included in the more narrowly defined aenigmatite or aenigmatite-rhönite group (e.g., Kunzmann 1999). Welshite is also the most eclectic mineral of the aenigmatite-sapphirine-surinamite group; it invariably contains significant Mn, Fe2+, and As, as well as Mg, Sb, Be, Al, and Si, constituents considered minimally essential to its formation (Hawthorne and Huminicki 2002). Moore (1967, 1971, 1978) originally introduced this mineral with the formula Ca4Mg2Fe2+2Sb1O4[Si8Be2O36], whereas Grew et al. (2001) deduced Ca5Mg2Mn2+3Fe2+2Sb1O4[Si8Be2O36] from a more detailed study of its chemistry using secondary ion-microprobe spectroscopy (SIMS) to measure Be. The ion-microprobe data gave 70% more Be than the amount predicted from crystallographic studies of other Be minerals of this group, makarochkinite, høgtuvaite, khmaralite, and surinamite, in which the amount of Be did not exceed 2.1 per formula unit of 40 O or, in surinamite, 2 per 36 O (Moore and Araki 1983; Barbier et al. 1999, 2002; Grew et al. 2005). These studies showed that 95–100% of the Be is found only at the most highly polymerized tetrahedral sites and Be-O-Be bridges are avoided. The failure to synthesize sapphirine with more than 2 Be per formula unit of 40 O is consistent with a crystallographic constraint on maximum Be content (Christy et al. 2002).