Brochantite, Cu₄SO₄(OH)₆: OD character, polytypism and crystal structures

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Abstract: Single-crystal X-ray diffraction studies of brochantite demonstrate its Order-Disorder (OD) character. The OD structures of the brochantite family can be described as built up by equivalent OD layers with symmetry Pn21m. Two MDO polytypes are possible in this family, and both have been identified in specimens of brochantite from various localities.

The MDO1 polytype corresponds to “normal” brochantite P121/a1, a = 13.140(2) Å, b = 9.863(2), c = 6.024(1), β = 103.16(3)°, whereas the newly discovered MDO2 polytype is monoclinic, P21/n11, a = 12.776(2) Å, b = 9.869(2), c = 6.026(1), α = 90.15(3)°. Given their polytypic relationships, the two MDO and MDO2 polytypes can be designated as brochantite-2M₁ and brochantite-2M₂, respectively.

The refined structure (R₁ = 0.049) of brochantite-2M₁ substantially agrees with the model of Cocco & Mazzi (1959) and confirms the assignment of the OH bands due to Schmidt & Lutz (1993). On the basis of the OD relationships between the two polytypes, a structural model for the newly discovered 2M₂ polytype was derived and subsequently refined up to R₁ = 0.062.

Key-words: brochantite, OD structures, 2M₁ and 2M₂ polytypes, structure refinement.

Introduction

Brochantite, Cu₄SO₄(OH)₆, is a widespread alteration phase, known in hundreds of mineralogical localities, typically deriving from the alteration of copper sulphides. Woods & Garrels (1986) discussed the formation and the stability of the most common basic copper salts, such as azurite, malachite, atacamite and brochantite, also in relation to various waters typically occurring at the Earth’s surface. They remarked that the above mentioned minerals react on the time-scale of days to the changing chemical environment and are therefore possibly useful as environmental indicators. Apart from its wide occurrence in natural environments, brochantite is a common constituent of the green patinas for med during the deterioration of copper and bronze manufactures (Gettens, 1970; Mattsson & Holm, 1982). Regarding this latter aspect, Mattsson & Holm (1982) remarked that brochantite is the most common alteration product in the urban/industrial environment.

The monoclinic symmetry of brochantite, P2₁/a, a = 13.05 Å, b = 9.83, c = 5.85, β = 103°22′, was determined by Palache (1939), using X-ray and morphological studies on crystals from Tsumeb. Lauro (1939, 1941) performed rotating crystal studies, that confirmed Palache’s (1939) data for the Tsumeb crystals, and reported the cell parameters a = 12.75 Å, b = 9.82, c = 5.94 for brochantite from Sa Duchessa mine, Sardinia.

The crystal structure of brochantite was firstly investigated, using the Tsumeb material, by Cocco & Mazzi (1959), who confirmed the space group P2₁/a and found the unit cell parameters a = 13.08 Å, b = 9.85, c = 6.02, β = 103.4°. In agreement with the previous studies, they noticed a constant (100) twinning, giving rise to a diffraction pattern which displayed orthorhombic symmetry and could be referred to a B centred pseudo-rhombohedral cell with A = a+c, B = b, C = c. Moreover, they made the following interesting observations on some peculiarities of the diffraction pattern:

- While all the spots with l = 2n are sharp, the spots with l = 2n+1 appear to be diffuse in a well defined direction, so that they fade out in the [201] (axis A) direction.
- Looking at the 0 KL reflections (indices given on the basis of the pseudo-rhombohedral cell), one can observe that, besides the “normal” space group absences, all reflections with K odd are absent (“non space group absences”).

Examining specimens of brochantite from Capo Calamita (Elba island, Tuscany, Italy), we observe that, whereas the reflections with l = 2n closely match the corresponding reflections of specimens from Tsumeb, the reflections with l = 2n+1 have different intensities.

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