Polysomatism in högbomite: The crystal structures of 10T, 12H, 14T, and 24R polysomes

CLIVIA HEJNY AND THOMAS ARMBRUSTER*

Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, Freiestr. 3, CH-3012 Bern, Switzerland

ABSTRACT

Högbomite is a closest-packed polysomatic mineral composed of spinel, T₃M₄O₉, and nolanite-like, TM₄O₇(OH), modules where T stands for tetrahedrally and M for octahedrally coordinated cations. The modules are stacked in an ordered fashion in various ratios. Single-crystal X-ray diffraction for a 24R and a 10T polysome and structure modeling for a 12H and 14T polysome have been applied to characterize different stacking variants.

Högbomite from a spinel-phlogopite schist at Corundum Creek (South Australia) with composition Mg₃.8Fe₃.2Zn₁.6Ti₁.0Al₁₈.₃O₃₈(OH)₂ is a 10T polysome with a = 5.723(1), c = 23.026(4) Å, space group P₃₁m, Z = 1. This polysome with the general formula T₃M₄O₉(OH)₂ is composed of an alternation of spinel (S) and nolanite-like (N) blocks stacked in the sequence NSSNS.

Högbomite from a Fe-Ti deposit at Liganga (Tanzania) with composition Mg₁₃.₅Fe₅.₆(Zn,Mn,Ni)₀.₂Ti₄.₇Al₄₁.₇(Cr,Ga)₀.₂O₉₀(OH)₆ is a 24R polysome with a = 5.7145(7), c = 55.056(5) Å, space group R₃m, Z = 1. The structure with the general formula T₃M₄O₉(OH)₂ is composed of two periodic alternation of the symbols S and T blocks.

The crystal structures of högbomite-12H, T₁₀M₂₄O₄₆(OH)₂, a = 5.7, c = 27.6 Å, space group P₆₃mc, Z = 1, and högbomite-14T, T₁₃M₂₄O₄₆(OH)₂, a = 5.7, c = 32.2 Å, space group P₃₃m, Z = 1, were modeled from the stacking principles of the known 6T, 8H, 10T, and 16H polysomes. The 12H and the 14T polysomes have stacking sequences NSSNSS and NSSNSS, respectively.

INTRODUCTION

The högbomite-mineral group comprises complex Al-Mg-Fe-Zn-Ti-oxides with a closest-packed oxygen array where the various group members have different oxygen stacking sequences. Crystal structures have been determined for högbomite-6H (Gatehouse and Grey 1982), zincohögbomite-8H (Armbuster 1998), and zincohögbomite-16H (Armbuster et al. 1998). In this nomenclature (Peacor 1967) the suffix nR, nH, or nT stands for n oxygen layers of ca. 2.3 Å thickness and R, H, or T for rhombohedral, hexagonal, or trigonal symmetry. The structure of högbomite has been explained in terms of two different modules, a spinel (S) and a nolanite (N) module (Gatehouse and Grey 1982; Armbuster 1998; Armbuster et al. 1998). The cubic closest-packed spinel module is composed of a layer with octahedrally coordinated cations (M), labeled O-layer, and a layer of tetrahedrally (T) and octahedrally (M) coordinated cations, labeled T₂-layer (Fig. 1). The O-layer has composition M₃O₄ and the T₂-layer has composition T₃M₄O₉. Thus, a complete spinel module, composed of one O- and one T₂-layer, has T₃M₄O₉ = 2 × TM₄O₉ stoichiometry. For högbomite the spinel module has composition Mg₄Al₂O₆, whereas for zincohögbomite the spinel module is equivalent to gehnite, ZnAl₂O₄. For Fe-rich högbomite the spinel module corresponds to hercynite, FeAl₂O₄. In the spinel module the octahedral positions are ideally occupied by Al and the tetrahedral positions by Mg, Zn, or Fe. The nolanite module is composed of a T₁-layer and an O-layer that is very similar to the one in spinel. One anion that links the O- and the T₁-layers is an OH group that is assigned to the T₁-layer. The composition of the T₁-layer is TMO₃(OH) and hence the stoichiometry of the nolanite module is TM₄O₇(OH). The nolanite subunit in högbomite has essential Ti⁴⁺ that may either reside on the octahedral sites of the T₁-layers (högbomite-8H; Gatehouse and Grey 1982; zincohögbomite-8H; Armbuster 1998) or in the O-layers as suggested for zincohögbomite-16H (Armbuster et al. 1998). A very simplified formula for a nolanite module in högbomite may be written as (Mg,Fe⁺⁺,Zn)Ti(Al,Fe⁺⁺)₄(OH)₆.

The packing of the oxygen layers in nolanite is characterized by alternating cubic (ABC) and hexagonal (ABA) packing, so that each nolanite module is associated with one intercalated oxygen layer of hexagonal closest-packed type. An alternative description of the oxygen stacking sequence uses the symbols “e” and “h” where “e” indicates that a specific oxygen layer has neighboring layers stacked in the cubic closest-packed fashion (ABC). Correspondingly, “h” stands for a layer where the layers above and below are of the same stacking type (e.g., the sequence is BCB or BAB). This latter nomenclature is very helpful to indicate the predominance of cubic closest-packed sequences and to assign the T₁ cation layers, which are between “ch” type sequences. In addition, the number of “h” layers and correspondingly the number of T₁ layers is responsible for the ratio of octahedral to tetrahedral sites in högbmites and for the number of hydroxyl ions.

The substitution of Ti⁴⁺ by Sn⁴⁺ in the nolanite-like module links högbomite group minerals to the closely related nigerite group. In nigerite (nigerite-6T: Arakcheeva et al. 1995; nigerite-24R: Grey and Gatehouse 1979) the octahedral position of the...