The crystal structure of ingersonite, Ca$_3$Mn$_2$Sb$_4$O$_{14}$, and its relationships with pyrochlore

PAOLA BONAZZI* AND LUCA BINDI

Dipartimento di Scienze della Terra, Università degli Studi di Firenze, via La Pira 4, I-50121 Firenze, Italy

ABSTRACT

The crystal structure of ingersonite, [Ca$_{9-y}$Mn$_{y+}$Fe$_{0.5}$]$_{2-0.5}$[Sb$_{3-2y}$Mg$_{2y}$]F$_{10-2y}$O$_{12.85}$, has been solved and refined in the space group $P3_{1}21$ [a = 7.28(2), c = 17.6(1) Å, V = 808.4(3) Å$^3$, Z = 3] to R = 2.32% for 2219 $F_0$ using MoKα X-ray data.

The structure of ingersonite is isomorphous with the synthetic weberite-3 polytype and related to the pyrochlore structure type. Both ingersonite and pyrochlore structures can be described as a sequence of pairs of polyhedral layers (named M and N), stacked along [111] and [001], respectively. In terms of the cation sites, M and N layers have general formula AB$_2$ and A,B, respectively, where B are the octahedral cations forming the B$_2$X$_6$ framework of the pyrochlore structure and A are the larger, interstitial cations forming eightfold polyhedra in pyrochlore.

In ingersonite, the M layers occur at $z$ ~ 1/6, 1/2, and 5/6. The B octahedra are occupied by Sb$^{5+}$ and share corners to form a pseudohexagonal tungsten bronze (HTB) motif with the A position occupied by octahedral Mn$^{2+}$ at the center of the pseudohexagonal rings. N layers occur at $z$ ~ 0, 1/3, and 2/3, with A = Ca and B = Sb$^{5+}$: Isolated B octahedra share 6 edges with 6 eightfold A polyhedra, to form a continuous sheet similar to the analogous layer in pyrochlore. The stacking of successive pairs of M and N layers in ingersonite is the same as in pyrochlore. Nonetheless, a difference in the relative position between M and N layers in ingersonite and pyrochlore is observed. The crystal-chemical relationships with other pyrochlore-related minerals are outlined.

Keywords: Ingersonite, crystal structure, chemical data, weberite-3 polytype, pyrochlore-related structure, X-ray diffraction data

INTRODUCTION

Ingersonite, ideally Ca$_3$Mn$_2$Sb$_4$O$_{14}$, was found on the dumps at the Längban mine, Värmland, Sweden, associated with fine-grained calcite and two opaque minerals, jacobsite and filipstadite (Dunn et al. 1988). According to these authors, ingersonite is trigonal, with $a$ = 7.287(3), $c$ = 17.679(9) Å, and $Z$ = 3, with the single-crystal diffraction pattern exhibiting a primitive lattice, Laue symmetry $3m$, and possible space groups including $P3_{1}1m$, $P312$, $P321$, $P31m$, $P3_{1}m1$, and $P3_21$.

The unit cell of ingersonite can easily be transformed by the matrix $[-2/3 -4/3 1/3 | 4/3 2/3 1/3 | -2/3 2/3 1/3]$ into a pseudo-cubic cell closely resembling that of the pyrochlore-type structure. Indeed, a wide variety of minerals having an ideal stoichiometry A$_2$B$_2$X$_6$Y (A = Ca, Na, K, Sr, Ba, Sn$^{2+}$, Pb$^{2+}$, REE$^{3+}$, Y, Sb$^{5+}$, Bi$^{3+}$, U$^{4+}$, X = O$^{2-}$, Y = O$^{2-}$, F, OH$^-$) possess a cubic pyrochlore-type structure (space group $Fd3m$). A relative ordering of the A cations and vacancies, or the accommodation of different cations with different coordination requirements can induce a reduction in symmetry below that of the conventional ideal pyrochlore structure. These relations, in combination with the A$_2$B$_2$X$_6$Y pyrochlore-like general formula, suggested that the ingersonite structure is a derivative of the pyrochlore structure type. Nonetheless, the synthetic Ca$_3$Sb$_4$O$_{14}$ compound crystallizes with both pyrochlore and orthorhombic weberite structure types (Brisse et al. 1972; Knop et al. 1980). It was hypothesized that the factors controlling a given antimonate to crystallize in one of these two competing structures (i.e., ionic radius and electronegativity of the A cation) define weberite and pyrochlore fields, with Ca$_3$Sb$_4$O$_{14}$ in the transition zone and Mn$_3$Sb$_4$O$_{12}$ well within the pyrochlore-type field (Knop et al. 1980). According to Scott (1990), the synthetic Mn$_3$Sb$_4$O$_{12}$ compound, however, crystallizes with a trigonal, pyrochlore-related structure (space group $P3_{2}1$) with unit-cell parameters $a$ = 7.1913(4), $c$ = 17.402(2) Å. On the other hand, two slightly different trigonal structures with space group $P3_{2}1$ (i.e. zirconolite-3T and weberite-3T) are found for (A,B)$_n$X$_2$ compounds having a similar unit cell ($a$ ~ 7 Å, $c$ ~ 17.18 Å). According to the IMA-approved nomenclature scheme (Bayliss et al. 1989), zirconolite-3T is the three-layered trigonal polytypoid of CaZrTi$_2$O$_7$ (Mazzi and Munno 1983), the others being zirconolite-3O (Mazzi and Munno 1983), the weberite-type polytypoid of CaZrTi$_2$O$_7$, and -2M (Gatehouse et al. 1981). Two additional polytypes, zirconolite-4M and -6T have been recently synthesized (Smith and Lumpkin 1993; Coelho et al. 1997). The mineral weberite, Na$_2$MgAlF$_7$, has orthorhombic symmetry (Giuseppetti and Tadini 1978) and represents, to our knowledge, the only natural member belonging to the weberite-type polytypic series; nonetheless, a few different polytypes are known among synthetic weberite-type fluorides and oxides, including 2M, 4M, 3T (Yakubovich et al. 1994), and

* E-mail: pbcry@geo.uni.it

0003-004X/07/0506–947S05.00/DOI: 10.2138/am.2007.2421 947