Armagmite, Mn$_{3+2}$[As$_{8}^{3+}$ (OH)$_{4}$ O$_{14}$][As$_{8}^{3+}$ O$_{18}$][CO$_{3}$], a fluorite derivative structure

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Abstract

Armagmite, Mn$_{3+2}$[As$_{8}^{3+}$ (OH)$_{4}$ O$_{14}$][As$_{8}^{3+}$ O$_{18}$][CO$_{3}$], $a_{t} = 13.491(2), c = 8.855(1)$Å, $Z = 1$, $P3$, was studied in detail by three-dimensional X-ray diffractometry. $R = 0.072$ ($R_{m} = 0.056$) for all 4012 non-equivalent reflections, and $R = 0.043$ for 2749 observable reflections above three times background error. X-ray diffraction data to sin$\theta$/λ = 0.80 (MoKa radiation, graphite monochromator) were collected on a Picker four-circle diffractometer, and the structure was solved by Patterson, Fourier, difference synthesis, and least-squares refinement techniques. The [CO$_{3}$] group was located on a difference synthesis, confirmed by electron probe analysis on select pure grains.

The structure is an anion-deficient fluorite derivative structure where $a_{t}$ (arm) = 2$\sqrt{2}$ $a_{i}$ (flu) and $c$ (arm) = $\sqrt{3}$ $a_{i}$ (flu) corresponding to a 4.94Å fluorite average edge. The fluorite stoichiometry is $X_{45}$, where $45X = 26$Mn$^{3+}$ + 18As$^{3+}$ + 1(CO$_{3}$) + 3δ(1), the cation vacancies occurring at $1/2\frac{1}{2}0$, etc.; and 96$\delta$ = 54 O(1) through O(9) + 42$\delta$(a) through $\delta$(i). Bond distance averages are 1[3]C–O 1.30, 1[3]As(1)–O 1.78, 1[3]As(2)–O 1.78, 1[3]As(3)–O 1.79, 1[6]Mn(1)–O 2.21, 1[6]Mn(2)–O 2.22, 1[6]Mn(3)–O 2.22, 1[6]Mn(4)–O 2.24, and 1[6]Mn(5)–O 2.22Å. The (CO$_{3}$) groups are disordered so O(10) is on the average only half-occupied. A cluster of composition Mn$_{3+2}$As$_{8}^{3+}$C$^{+}$O$_{3}$ can be extracted which is related to the arrangement in the Fe$^{2+}$ oxyphosphate sheet of mitridatite, which also locally is a fluorite derivative structure. Mn(1), Mn(2), Mn(3), and Mn(5) are distorted octahedra, Mn(4) is a distorted trigonal prism, and As(1), As(2), and As(3) are distorted trigonal pyramids. Local environments in armagmite are similar to those in magnussonite, a related structure, but central Mn$^{3+}$ in armagmite is missing.

Introduction

Armagmite, originally described by Aminoff and Mauzelius (1920), occurred as a rare late-stage mineral in basic, reduced veins with calcite and barite from Langban, Sweden. These authors interpreted the original analysis as including the presence of an admixed carbonate, and deduction of these impurities led to the relatively simple composition Mn$_{3+2}$ (AsO$_{5}$)$_{2}$. Despite the simple composition the cell contains nine formula units, and question arose regarding the possible space groups (originally listed as rhombohedral) despite the trigonal development of the crystals. Our study shows that the extinction criteria definitely belong to a trigonal group, specifically $P3$, and that the compound does not possess such a simple composition.

Work on armagmite's structure was initiated by the senior author ten years ago, but the problem was abandoned owing to its inherent difficulty. Not until our study on the compositionally-related magnussonite (Moore and Araki, 1979) did we discover a relationship between these phases and the relatively simple and versatile fluorite structure type. This relationship, coupled with the presence of arsenite groups which include lone pair electrons, revitalized our interest in the problem.

Experimental section

A small fragment of Flink unknown U71 (from the Swedish Natural History Museum) showed pale brown hexagonal prisms embedded in dolomite–haussmannite rock. It was investigated fourteen years ago and shown to be identical with armagmite through single-crystal X-ray and powder photography. More recently, a fragment of specimen R5795 (National Museum of Natural History, Smithsonian