Quadratite, AgCdAsS$_2$: Chemical composition, crystal structure, and OD character

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ABSTRACT

A re-investigation of the crystal structure of quadratite, ideally AgCdAsS$_2$, was undertaken using a single crystal from the type locality, Lengenbach, Binntal, Switzerland. The average of five electron microprobe analyses led to the empirical formula (Ag$_{0.995}$Cd$_{0.005}$Pb$_{0.25}$Cu$_{0.001}$Ti$_{0.05}$Mn$_{0.05}$Fe$_{0.05}$Zn$_{0.02}$Cr$_{0.001}$)$_2$-1.954(As$_{0.95}$Sb$_{0.05}$)$_2$-0.953S$_3$. A single-crystal structure refinement ($R = 4.84\%$ for 558 observed reflections) shows that quadratite crystallizes in the space group $P4_222$ and exhibits an atomic arrangement similar to that of the recently approved new mineral manganouadratite, AgMnAsS$_2$. Like manganouadratite, quadratite adopts a galena-derivative framework, with metal atoms occupying all the available octahedral interstices, although only M1 and M2 cations, occupied mainly by Cd, adopt a fairly regular octahedral coordination; the M3 cation, occupied by Ag, is located outside the center cavity in a square-pyramidal coordination, whereas Pb at the split position M3' coordinates six S atoms. Arsenic also adopts a $3 + 3$ asymmetrical coordination, thus forming the AsS$_3$ pyramidal groups that typically occur in sulfosalts.

The structure can be also described as a stacking of BAB slabs [A: (CdAg)CdS$_3$ atomic plane; B: (Ag,Pb)AsS$_3$ atomic plane] along [001]. The rectangular unit cell of these slabs is oriented diagonally to the a axes of quadratite and consecutive slabs are related via interlayer twofold rotation operations parallel either to [100] or to [010]. This ambiguity leads to an OD structure with various possible stacking sequences, from which the tetragonal space group $P4_222$ was observed.

Keywords: Quadratite, Cd-sulfosalts, crystal structure, chemical composition, OD character, Lengenbach

INTRODUCTION

Quadratite, ideally AgCdAsS$_2$, was first found as minute quadratic crystals within cavities of the well-known Lengenbach dolomite, Binntal, Switzerland, in 1989 and described as a new mineral species only in 1998 (Graeser et al. 1998), when suitable material was found for physical characterization and diffraction data. On the basis of a single-crystal investigation (Weissenberg and precession methods), Graeser et al. determined that the mineral was tetragonal, with $a = 5.499(5)$, $c = 33.91(4)$ Å, space group $I4_{1}/amd$. An approximate model of the crystal structure of quadratite was then obtained by Berlepsch et al. (1999), by assuming the apparent $I4_{1}/amd$ crystal symmetry as the result of the superposition of two enantiomorphic structures, having space groups $P4_222$ and $P4_222$, respectively. According to their model, quadratite can be described as a galena-based derivative framework composed of warped layers parallel to (001) with cations located in distorted octahedral coordinations. Possibly owing to twinning or order-disorder phenomena in quadratite crystals, S atoms are disordered on split positions.

Recently, the new mineral manganouadratite (Bonazzi et al. 2012) showing a close similarity of formula (AgMnAsS$_3$) and unit-cell dimensions [$a = 5.4496(5)$, $c = 32.949(1)$] with quadratite has been found in the Uchucchacua polymetallic deposit, Peru. Manganouadratite crystallizes in the space group $P4_222$ and exhibits a galena-derivative framework, with S atoms arranged in a cubic closest-packing array with metal atoms occupying all available octahedral interstices. Only the Mn$^{2+}$ cations, however, adopt an octahedral coordination, whereas Ag$^+$ and As$^{3+}$ are located outside the center cavities, forming asymmetrical coordination polyhedra, AgS$_3$ and AsS$_3$, respectively. To verify whether or not quadratite is isostructural with manganouadratite or whether or not quadratite is isostructural with manganouadratite or whether or not it possesses a different symmetry involving an alternative distribution of the metals within the sulfur close packed structure, a re-investigation of the crystal structure of quadratite was undertaken.

CHEMICAL COMPOSITION

The crystal fragment of quadratite used for the structural study was analyzed with a JEOL JXA-8200 electron microprobe. Major and minor elements were determined at 15 kV accelerating voltage and 30 nA beam current, with 15 s as counting time. For the wavelength-dispersion analyses the following lines were used: AgK$_\alpha$, CuK$_\alpha$, PbM$_{4,5}$, CdK$_\alpha$, TlM$_\alpha$, MnK$_\alpha$, FeK$_\alpha$, ZnK$_\alpha$, CrK$_\alpha$, SbL$_{3,4}$, AsL$_{3,4}$, and SK$_\alpha$. The standards employed were: Ag-pure element (Ag), Cu-pure element (Cu), galena (Pb), Cd-pure element (Cd), synthetic TiTe (Ti), synthetic MnS (Mn), pyrite (FeS), synthetic ZnS (Zn), Cr-pure element (Cr), synthetic Sb$_2$S$_3$ (Sb), and synthetic GaAs (As). The crystal fragment was found to

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