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LETTER

Crystal structure of uchucchacuaite, $AgMnPb_3Sb_5S_{12}$, and its relationship with ramdohrite and fizélyite

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ABSTRACT

Uchucchacuaite, ideally $AgMnPb_3Sb_5S_{12}$, was originally reported as orthorhombic, with possible space group *Pmmm*, *P*222, or *Pmm*2, and unit-cell parameters $a = 12.67$, $b = 19.32$, and $c = 4.38$ Å obtained from powder X-ray diffraction data (Moëlo et al. 1984a). Using single-crystal X-ray diffraction, we examined two uchucchacuaite samples, one from the type locality, Uchucchacua, Peru, and the other from Hokkaido, Japan (designated as R100213 and R070760, respectively). Our results show that uchucchacuaite is isostructural with ramdohrite and fizélyite, with monoclinic symmetry ($P2_1/n$) and the unit-cell parameters $a = 19.3645(11)$, $b = 12.7287(8)$, $c = 8.7571(6)$ Å, $\beta = 90.059(3)°$ for R100213 and $a = 19.3462(7)$, $b = 12.7251(5)$, $c = 8.7472(3)$ Å, $\beta = 90.017(2)°$ for R070760. Both samples are pervasively twinned and the twin refinements yielded the final R_1 factors of 0.037 and 0.031 for R100213 and R070760, respectively. The chemical compositions determined from electron microprobe analysis are $Ag_{0.99}(Mn_{0.92}Pb_{0.03}Sb_{0.02}Bi_{0.01})_{\Sigma=0.98}Pb_{3.00}Sb_{5.00}S_{12.00}$ for R100213 and $Ag_{1.00}(Mn_{0.82}Sb_{0.11}Ag_{0.04}Bi_{0.02})_{\Sigma=0.99}Pb_{2.98}Sb_{5.00}S_{12.00}$ for R070760. The key structural difference among uchucchacuaite, ramdohrite, and fizélyite lies in the cations occupying the M2 site, which can be expressed with a general structural formula as $Ag(M^{2+}_{2y}Ag_{½-y}Sb_{½-y})Pb_3Sb_5S_{12}$, where M^{2+} represents divalent cations with $0 \leq y \leq ½$. From the current list of IMA-defined minerals, we consider M = Cd with $y = 0.125$ for ramdohrite, M = Pb with $y = 0.25$ for fizélyite, and M = Mn with $y = 0.5$ for uchucchacuaite. Associated with the variation in the average M2 cation size from fizélyite (1.078 Å) to ramdohrite (0.955 Å) and uchucchacuaite (0.83 Å) is the significant decrease in the average M2-S bond distance from 2.917 to 2.834, and 2.654 Å, respectively, as well as corresponding variations in the unit-cell *b* dimension from ~13.23 to 13.06 and 12.73 Å.

Keywords: Uchucchacuaite, fizélyite, ramdohrite, andorite series, sulfosalts, crystal structure, single-crystal X-ray diffraction

INTRODUCTION

Uchucchacuaite, $AgMnPb_3Sb_5S_{12}$, belongs to the Sb-rich andorite subgroup in the lillianite homeotypic series of Pb-Ag-Sb-Bi sulfosalts (Moëlo et al. 2008). A general chemical formula for the andorite subgroup can be expressed as $Ag_xPb_{3-2x}Sb_{2+x}S_6$, with possible substitution of Mn/Cd for Pb and Cu for Ag. Minerals within this subgroup, which are usually classified based on the percentage of the andorite component ($And_{x\%}$), (Moëlo et al. 2008), include uchucchacuaite (And_{50}), fizélyite $Ag_5Pb_{14}Sb_{21}S_{48}$ ($And_{62.5}$), ramdohrite $CdAg_{5.5}Pb_{12}Sb_{21.5}S_{48}$ ($And_{68.75}$), andorite IV $Ag_{15}Pb_{18}Sb_{47}S_{96}$ ($And_{93.75}$), andorite VI $AgPbSb_3S_6$ (And_{100}), and roshchinite $(Ag,Cu)_{19}Pb_{10}Sb_{51}S_{96}$ ($And_{118.75}$). Depending on the chemical composition, the *c* periodicity in this subgroup is a multiple *n* of ~4.36 Å. The reported data show $n = 1$ for uchucchacuaite (Moëlo et al. 1984a), $n = 2$ for fizélyite (Moëlo et al. 1984b; Yang et al. 2009) and ramdohrite (Makovicky and Mumme 1983), $n = 4$ for andorite IV (Donnay and Donnay 1954; Moëlo et al. 1984b) and roshchinite (Spiridnov et al. 1990), and $n = 6$ for andorite VI (Donnay and Donnay 1954; Sawada et al. 1987).

Uchucchacuaite was first discovered in Uchucchacua, Peru (Moëlo et al. 1984a), and later in Hokkaido, Japan (Matsubara and Miyawaki 2006). According to Moëlo et al. (1984a), uchucchacuaite from Peru has the composition $Ag_{0.98}(Mn_{0.91}Fe_{0.06})_{\Sigma 0.97}Pb_{3.04}Sb_{5.09}(S_{11.93}Se_{0.07})_{\Sigma 12}$. Its X-ray powder pattern was indexed on the basis of it being in the andorite series with orthorhombic symmetry, possible space group *Pmmm, P*222, or *Pmm*2, and unit-cell parameters $a = 12.67$, $b = 19.32$, $c = 4.38$ Å. Moëlo et al. (1984a) further suggested an ordered distribution of Pb and Mn in the structure. Since then, no detailed crystallographic study has been reported for this mineral and its structural relationship with other minerals in the andorite series has remained unaddressed. Based on single-crystal X-ray diffraction data, this study presents the first structure determination of uchucchacuaite and demonstrates that it is isotypic with ramdohrite and fizélyite, with monoclinic symmetry ($P2_1/n$) and its *c* dimension twice that reported by Moëlo et al. (1984a).

EXPERIMENTAL PROCEDURES

Two uchucchacuaite samples were used in this study: one from the type locality Uchucchacua, Peru (RRUFF project collection, R100213; http://rruff.info/R100213), and the other from Hokkaido, Japan (RRUFF project collection, R070760; http://rruff.info/R070760). The sample compositions were analyzed on

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a Cameca SX100 electron microprobe with an accelerating potential of 15 kV and a beam current of 20 nA. Standards include galena for Pb and S, stibnite for Sb, synthetic $MnTa_2O_6$ for Mn, and synthetic $AgBiS_2$ for Ag and Bi. The resultant chemical formulas were calculated from the average compositions of 15 analysis points for each sample by normalizing S atoms to 12 while maintaining the total charge balance, yielding $Ag_{0.99}(Mn_{0.92}Pb_{0.03}Sb_{0.02}Bi_{0.01})_{\Sigma=0.98}Pb_{3.00}Sb_{5.00}S_{12.00}$ for R100213 and $Ag_{1.00}(Mn_{0.82}Sb_{0.11}Ag_{0.04}Bi_{0.02})_{\Sigma=0.99}Pb_{2.98}Sb_{5.00}S_{12.00}$ for R070760.

On the basis of optical examination and X-ray diffraction peak profiles, a nearly equi-dimensional crystal (~0.04 × 0.04 × 0.04 mm for R100213 and ~0.05 × 0.05 × 0.04 mm for R070760) was cut from a fragment (the rest was used for microprobe analysis) from each sample and mounted on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized Mo*Kα* radiation. The detailed experimental procedures were similar to those described by Yang et al. (2009). Reflections with $I > 2\sigma(I)$ were indexed based on a monoclinic unit cell (Table 1). No satellite or super-lattice reflections were observed. Observed systematic absences of reflections for both samples indicate the unique space group $P2_1/n$. The structure was solved and refined using the program SHELX97 (Sheldrick 2008). Both samples are pervasively twinned with the twin axis along [100]. Without the twin refinement, the R_1 factors were 0.13 and 0.11 for R100213 and R070760, respectively, which were reduced to 0.037 and 0.031 after the twin refinement (Table 1). All atoms were refined with anisotropic displacement parameters. To facilitate the comparison with ramdohrite and fizélyite, the labeling scheme of atomic sites for uchucchacuaite follows that given by Yang et al. (2009). An initial structure refinement revealed that all atomic sites in both samples had nearly ideal site occupancies, except the M2 site, which appeared to require a small amount of atom(s) heavier than Mn for a full occupancy, consistent with our chemical analysis. Hence, for simplicity, we only refined the M2 site occupancy with Mn against (Sb+Ag) with the site occupancy of Sb equaling that of Ag in the subsequent refinements and fixed the remaining site occupancies to their ideal values (=1.0), which produced a structural formula of $Ag(Mn_{0.902\pm2}Ag_{0.049}Sb_{0.049})Pb_3Sb_5S_{12}$ for R100213 and $Ag(Mn_{0.918\pm2}Ag_{0.041}Sb_{0.041})Pb_3Sb_5S_{12}$ for R070760. Final refined atomic coordinates and isotropic displacement parameters are listed in Table 2 and selected bond lengths in Table 3. CIF[1] files for the two samples are on deposit.

RESULTS AND DISCUSSION

Unit-cell parameters

Our data, on the one hand, clearly demonstrate that uchucchacuaite is monoclinic, with a *c* dimension of ~8.75 Å (*n* = 2), rather than 4.38 Å (*n* = 1), as reported by Moëlo et al. (1984a) from X-ray powder diffraction data, although Pažout and Dušek (2010) found such a cell (*n* = 1) to be true for a mineral phase of the lillianite homologues with the composition $Ag_{0.71}Pb_{1.52}Bi_{1.32}Sb_{1.45}S_6$. The unit cell presented in the original definition paper is, therefore, a strong sub-cell, characteristic of minerals in the lillianite-andorite homeotypic series (Makovicky 1997). On the other hand, noticeably, the *b* dimension of uchucchacuaite is 2.7% and 3.8% shorter, respectively, than that of ramdohrite and fizélyite (Table 1, also see Moëlo et al. 1984a, 1984b). Thus, the *b* dimension, as well as the unit-cell volume, in ramdohrite-type material appears to be very sensitive to the average cation size in the M2 site, as discussed below. However, the decrease in the *b* dimension from fizélyite to ramdohrite and uchucchacuaite may not be continuous, as fizélyite crystals from both Kisbánya (Romania) and Potosi (Bolivia) have been found to exhibit exsolutions of ramdohrite and a (Mn,Fe)-rich variety of ramdohrite (Moëlo et al. 1984b, 1989), which, according to this study, is presumably uchucchacuaite.

Crystal structure

Uchucchacuaite is isostructural with ramdohrite (Makovicky and Mumme 1983) and fizélyite (Yang et al. 2009). A basic structural feature of ramdohrite-type minerals is that they consist of octahedral slabs parallel to (100) that are linked together by distorted AgS_4 tetrahedra, $M2S_6$ octahedra, and PbS_8 polyhedra (Pb1 and Pb2) (Fig. 1). The octahedral slabs are formed by two kinds of rods extending along ***c***: The A rod contains four edge-sharing SbS_6 octahedra (Sb1, Sb2, Sb3, and Sb4), whereas the B rod is made of only two edge-sharing octahedra (Sb5 and M1). The five SbS_6 octahedra are all considerably distorted, with each formed by three short and three long Sb-S bonds (Table 3). The three longer Sb-S bonds within each SbS_6 octahedron are principally due to the presence of lone electron pairs, resulting in so-called "*lone electron pair micelles*" (Makovicky 1997; Gibbs et al. 2011). There are two types of lone-electron-pair micelles in ramdohrite-type materials. The larger micelles with four lone pairs of electrons are confined within the A rod and the smaller ones with two lone pairs of electrons within the B rod, as described for ramdohrite by Makovicky and Mumme (1983).

TABLE 1. Summary of crystal data and refinement results for uchucchacuaite, ramdohrite, and Ag-excess fizélyite

	Uchucchacuaite (Peru, R100213)	Uchucchacuaite (Japan, R070760)	Ramdohrite	Fizélyite
IMA-defined chemical formula	$AgMnPb_3Sb_5S_{12}$	$AgMnPb_3Sb_5S_{12}$	$CdAg_{5.5}Pb_{12}Sb_{21.5}S_{48}$	$Ag_5Pb_{14}Sb_{21}S_{48}$
Effective structural formula	$Ag(M2)^*Pb_3Sb_5S_{12}$	$Ag(M2)Pb_3Sb_5S_{12}$	$Ag(M2)Pb_3Sb_5S_{12}$	$Ag_{1.21}(M2)Pb_{2.88}Sb_{5.12}S_{12}$
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	19.3645(11)	19.3462(7)	19.24	19.2767(6)
b (Å)	12.7287(8)	12.7251(5)	13.08	13.2345(4)
c (Å)	8.7571(6)	8.7472(3)	8.73	8.7230(3)
β (°)	90.059(3)	90.017(2)	90.28	90.401(2)
V (Å^3)	2158.5(2)	2153.4(1)	2197.0	2225.3(1)
Z	4	4	4	4
ρ_{calc} (g/cm^3)	5.487	5.498		5.644
λ (Å)	0.71073	0.71073		0.71073
μ (mm^{-1})	32.338	32.179		34.49
2θ range for data collection	≤65.26	≤65.16		≤59.14
No. of reflections collected	29354	32560		31150
No. of independent reflections	7874	7829		6237
No. of reflections with $I > 2\sigma(I)$	6144	6719	1613	4272
No. of parameters refined	203	203		236
R_{int}	0.053	0.038		0.068
Final R_1, wR_2 factors [$I > 2\sigma(I)$]	0.037, 0.050	0.032, 0.053	~0.20	0.041, 0.076
Final R_1, wR_2 factors (all data)	0.052, 0.063	0.045, 0.056		0.068, 0.084
Goodness-of-fit	0.983	1.052		1.064
Twin law	$(100/0\bar{1}0/00\bar{1})$	$(100/0\bar{1}0/00\bar{1})$	$(100/0\bar{1}0/00\bar{1})$	
Twin ratio	0.50/0.50	0.69/0.31	0.86/0.14	
Reference	(1)	(1)	(2)	(3)

Note: References: (1) this study; (2) Makovicky and Mumme (1983); (3) Yang et al. (2009).
* M2 = $(Mn_{0.90}Ag_{0.05}Sb_{0.05})$ for R100213, $(Mn_{0.92}Ag_{0.04}Sb_{0.04})$ for R070760, $(Ag_{0.50}Sb_{0.50})$ for ramdohrite, and $(Pb_{0.57}Ag_{0.33}Sb_{0.10})$ for fizélyite.

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[1] Deposit item AM-11-037, CIFs and complete Table 2. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 2. Atomic coordinates and isotropic displacement parameters of uchucchacuaite

Atom	*x*	*y*	*z*	U_{eq}	*x*	*y*	*z*	U_{eq}
	Uchucchacuaite from Peru (R100213)				**Uchucchacuaite from Japan (R070760)**			
Pb1	0.25569(2)	0.90189(3)	0.38932(4)	0.0233(1)	0.25586(2)	0.90166(2)	0.38972(3)	0.0227(1)
Pb2	0.24831(2)	0.91430(3)	–0.09676(4)	0.0260(1)	0.24825(2)	0.91460(2)	–0.09672(3)	0.0248(1)
M1*	0.05187(2)	0.90209(2)	0.62985(4)	0.0217(1)	0.05180(1)	0.90146(2)	0.62997(3)	0.0202(1)
M2*	0.13248(6)	0.14672(8)	0.1263(2)	0.0221(4)	0.13211(5)	0.14680(7)	0.1259(1)	0.0218(3)
Ag	0.14180(4)	0.17609(7)	0.6230(1)	0.0433(2)	0.14163(3)	0.17629(6)	0.62300(8)	0.0426(2)
Sb1	0.35239(3)	0.12500(4)	0.64424(7)	0.0186(1)	0.35223(2)	0.12524(4)	0.64424(5)	0.0170(1)
Sb2	0.44416(3)	0.86816(4)	0.61507(7)	0.0174(1)	0.44411(2)	0.86875(3)	0.61565(5)	0.0160(1)
Sb3	0.12858(3)	0.64468(4)	0.38406(8)	0.0166(1)	0.12878(2)	0.64473(3)	0.38365(5)	0.0156(1)
Sb4	–0.05365(3)	0.64186(4)	0.63757(7)	0.0183(1)	0.05359(2)	0.64154(4)	0.63753(5)	0.0165(1)
Sb5	0.05504(3)	0.88068(4)	0.14369(7)	0.0172(1)	0.05487(2)	0.88067(3)	0.14325(5)	0.0153(1)
S1	0.3962(1)	0.9938(2)	–0.1679(2)	0.0185(5)	0.3963(1)	0.9942(2)	–0.1673(2)	0.0181(4)
S2	–0.0075(1)	0.7504(2)	0.8472(2)	0.0218(5)	0.0074(1)	0.7498(2)	0.8477(2)	0.0198(4)
S3	0.2355(1)	0.0451(2)	–0.3533(3)	0.0197(4)	0.2353(1)	0.0456(1)	–0.3535(2)	0.0187(3)
S4	0.3393(1)	0.7656(2)	0.6039(3)	0.0194(5)	0.3393(1)	0.7662(1)	0.6038(2)	0.0184(3)
S5	0.1024(1)	0.9892(2)	0.9397(3)	0.0194(5)	0.1024(1)	0.9889(2)	0.9395(2)	0.0191(4)
S6	0.1647(1)	0.7618(2)	0.5901(3)	0.0184(5)	0.1649(1)	0.7618(1)	0.5903(2)	0.0175(3)
S7	0.4015(1)	0.0004(2)	0.4296(3)	0.0182(5)	0.4014(1)	0.0006(1)	0.4299(2)	0.0160(3)
S8	–0.0172(1)	0.7646(2)	0.4299(2)	0.0185(5)	0.0171(1)	0.7644(1)	0.4302(2)	0.0174(4)
S9	0.2558(1)	0.0607(2)	0.1338(2)	0.0186(4)	0.2557(1)	0.0608(1)	0.1344(2)	0.0176(3)
S10	–0.1669(1)	0.7225(2)	0.6553(3)	0.0183(5)	0.1670(1)	0.7216(1)	0.6544(2)	0.0179(4)
S11	0.0933(1)	0.0070(2)	0.3350(3)	0.0197(5)	0.0930(1)	0.0065(1)	0.3359(2)	0.0199(4)
S12	0.1598(1)	0.7668(2)	0.1677(3)	0.0179(5)	0.1597(1)	0.7670(1)	0.1672(2)	0.0166(3)

* M1 = Pb for both structures. M2 = 0.902(2) Mn + 0.049 Ag + 0.049 Sb for R100213 and 0.918(2) Mn + 0.041 Ag + 0.041 Sb for R070760.

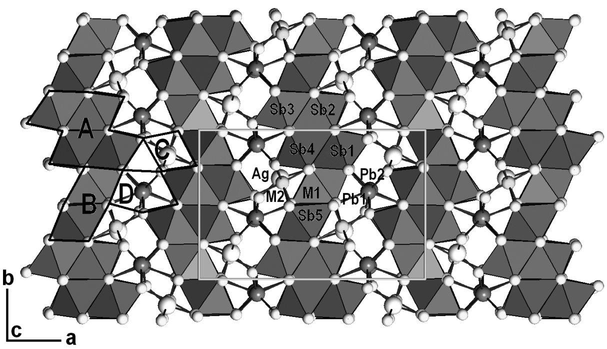

FIGURE 1. Crystal structure of uchucchacuaite viewed along the *c* axis. Outline A = edge-sharing SbS_6 octahedral rods, outline B = edge-sharing Sb5 and M1 octahedral rods, outline C = alternating AgS_4 tetrahedra and $M2S_6$ octahedra, and outline D = Pb1 and Pb2 polyhedral chains.

The key structural difference among uchucchacuaite, ramdohrite, and fizélyite lies in the cations occupying the M2 site. This site is occupied by ($Pb^{2+} + Ag^+ + Sb^{3+}$) in Ag-excess fizélyite (Yang et al. 2009), ($Sb^{3+} + Ag^+$) in ramdohrite (Makovicky and Mumme 1983) [or presumably by Cd^{2+} detected by Moëlo et al. (1989)], and Mn^{2+} in uchucchacuaite. For ideal fizélyite, the M2 site should contain (0.50 Pb + 0.25 Ag + 0.25 Sb) (Makovicky and Mumme 1983). The ordering of Mn into the M2 site in uchucchacuaite was speculated by Makovicky and Mumme (1983) based on the ramdohrite structure. Associated with the change in the average M2 cation size from fizélyite (1.078 Å) to ramdohrite (0.955 Å) and uchucchacuaite (0.83 Å) is the significant decrease in the average M2-S bond distance from 2.917 to 2.834 and 2.654 Å, respectively. Evidently, this change controls the variation of the unit-cell *b* dimension in these minerals. With the decrease in the average M2 cation size, the M2 octahedron becomes less distorted, as measured by the indexes of the octahedral angle variance (OAV) and octahedral quadratic elongation (OQE) (Robinson et al. 1971). The OAV and OQE values are 96.4 and 1.028, respectively, for the M2 octahedron in fizélyite, 53.5 and 1.016 in ramdohrite, and 38.7 and 1.012 in uchucchacuaite.

It should be noted that the M1 site in uchucchacuaite and ramdohrite is fully filled with Pb, but it has a mixed occupancy of (0.88 Pb + 0.12 Sb) in Ag-excess fizélyite (Yang et al. 2009). In ideal fizélyite, nonetheless, this site should contain Pb only, as in ramdohrite and uchucchacuaite.

Based on the above discussion, it becomes obvious that it is the makeup of the M2 site that defines the chemical and structural differences among ramdohrite, fizélyite, and uchucchacuaite. Accordingly, we present a general structural formula for ideal ramdohrite-type minerals as follows:

$$Ag(M^{2+}_{2y}Ag_{½-y}Sb_{½-y})Pb_3Sb_5S_{12}$$

where M^{2+} represents divalent cations and $0 \leq y \leq ½$. From the current list of mineral chemical formulas defined by the International Mineralogical Association, we consider M = Cd with $y = 0.125$ for ramdohrite, M = Pb with $y = 0.25$ for fizélyite, and M = Mn with $y = 0.5$ for uchucchacuaite. From this general chemical formula for the ramdohrite-type minerals, one may postulate the possible existence of other M^{2+} cations, in addition to Cd, Pb, and Mn, as a major component in the M2 site, such as Fe^{2+}. In fact, one of the fizélyite samples (sample no. 4 from Bohemia, Czech Republic) examined by Kašpar et al. (1983) contains 0.14 Fe^{2+} (based on 12 S atoms or 0.43 wt% Fe) and no Mn^{2+}.

Another interesting question that immediately follows regards the variation range of the *y* value for each ramdohrite-type mineral. For ramdohrite, Moëlo et al. (1984b, 1989) uncovered that this mineral always contains an appreciable concentration of Cd, as high as 1.6 wt% in some samples, pointing to a specific crystal-chemical role of Cd in stabilizing its structure. This means that ramdohrite without the M cation ($y = 0$), namely $Ag(Ag_{0.5}Sb_{0.5})Pb_3Sb_5S_{12}$, may not be stable under natural conditions. Therefore,

TABLE 3. Selected bond lengths (Å) in uchucchacuaite

	R100213	R070760		R100213	R070760
Pb1-S3	2.926(2)	2.925(2)	Sb1-S3	2.482(2)	2.480(2)
Pb1-S10	2.994(2)	2.988(2)	Sb1-S1	2.493(2)	2.495(2)
Pb1-S9	3.016(2)	3.015(2)	Sb1-S7	2.637(2)	2.634(2)
Pb1-S4	3.026(2)	3.013(2)	Sb1-S6	2.925(2)	2.919(2)
Pb1-S6	3.064(2)	3.057(2)	Sb1-S12	3.286(2)	3.275(2)
Pb1-S7	3.109(2)	3.105(2)	Sb1-S2	3.402(2)	3.395(2)
Pb1-12	3.188(2)	3.192(2)			
Pb1-S11	3.450(2)	3.454(2)			
Pb2-S9	2.751(2)	2.752(2)	Sb2-S4	2.415(2)	2.414(2)
Pb2-S3	2.807(2)	2.808(2)	Sb2-S7	2.480(2)	2.478(2)
Pb2-S5	3.000(2)	2.992(2)	Sb2-S1	2.653(2)	2.647(2)
Pb2-S1	3.101(2)	3.100(2)	Sb2-S2	2.943(2)	2.941(2)
Pb2-S10	3.255(2)	3.242(2)	Sb2-S8	3.319(2)	3.317(2)
Pb2-S12	3.439(2)	3.435(2)	Sb2-S7	3.448(2)	3.443(2)
Pb2-S4	3.684(2)	3.679(2)			
Pb2-S6	3.728(2)	3.725(2)			
M1-S8	2.813(2)	2.806(2)	Sb3-S6	2.443(2)	2.444(2)
M1-S6	2.843(2)	2.841(2)	Sb3-S9	2.487(2)	2.481(2)
M1-S2	2.946(2)	2.943(2)	Sb3-S12	2.525(2)	2.522(2)
M1-S11	3.016(2)	3.007(2)	Sb3-S1	3.178(2)	3.172(2)
M1-S11	3.056(2)	3.051(2)	Sb3-S8	3.234(2)	3.233(2)
M1-S5	3.089(2)	3.086(2)	Sb3-S7	3.355(2)	3.350(2)
M2-S4	2.580(3)	2.579(2)	Sb4-S10	2.426(2)	2.423(2)
M2-S10	2.621(3)	2.637(2)	Sb4-S2	2.464(2)	2.465(2)
M2-S9	2.627(2)	2.630(2)	Sb4-S8	2.500(2)	2.496(2)
M2-S5	2.651(3)	2.651(2)	Sb4-S7	3.253(2)	3.251(2)
M2-S11	2.661(3)	2.671(2)	Sb4-S1	3.328(2)	3.322(2)
M2-S2	2.762(3)	2.758(2)	Sb4-S1	3.594(2)	3.584(2)
Ag1-S3	2.472(2)	2.468(2)	Sb5-S11	2.437(2)	2.439(2)
Ag1-S8	2.571(2)	2.567(2)	Sb5-S5	2.438(2)	2.433(2)
Ag1-S4	2.674(3)	2.675(2)	Sb5-S12	2.502(2)	2.499(2)
Ag1-S10	2.801(2)	2.796(2)	Sb5-S8	3.229(2)	3.230(2)
			Sb5-S2	3.310(2)	3.302(2)
			Sb5-S5	3.545(2)	3.541(2)

we suggest $0 < y \leq 0.125$ for ramdohrite. However, because the ionic radius of Cd^{2+} (0.95 Å) is nearly identical to the average value of $(Ag^+ + Sb^{3+})$ (0.955 Å), we cannot rule out the existence of ramdohrite with $y > 0.125$ in some environments.

The y values for most fizélyite samples documented in the literature fall between 0.2 and 0.25 (e.g., Moëlo et al. 1984b, 1989; Weiner and Hochleitner 1984). Owing to its great structural flexibility and various chemical substitution mechanisms (Moëlo et al. 1984b; Yang et al. 2009), it is likely that fizélyite with $y < 0.2$ or > 0.25 may also exist. In fact, Yang et al. (2009) determined the structure of an Ag-excess fizelyite, in which the M2 site contains (0.56 Pb + 0.10 Sb + 0.33 Ag) or $y = 0.28$ for Pb.

In contrast to ramdohrite and fizélyite, all uchucchacuaite samples examined thus far (Moëlo et al. 1984a; this study) exhibit a nearly ideal y value (=0.5) if we treat the small amount of Fe as Mn. This observation indicates that there may be only a very limited substitution between Mn^{2+} and $(Sb^{3+} + Ag^+)$, presumably due to the difference in the bonding between Mn^{2+}-S and $(Sb^{3+} + Ag^+)$-S (Makovicky 1997). The fact that fizélyite has been observed to display exsolutions of a (Mn,Fe)-rich variety of ramdohrite (Moëlo et al. 1984b, 1989) lends further support to our inference above. Remarkably, Liu et al. (1994) reported the synthesis of uchucchacuaite in the Ag_2S-MnS-PbS-Sb_2S_3 system between 300 and 500 °C and its unit-cell parameters $a = 13.08(1)$, $b = 19.46(1)$, and $c = 4.27$ Å, calculated from X-ray powder diffraction data by assuming an andorite-type structure. They claimed that uchucchacuaite forms a complete solid-solution series with andorite. However, because uchucchacuaite is not isostructural with either andorite IV or andorite VI, we think that the conclusion of Liu et al. (1994) is questionable and their synthetic products need to be reexamined carefully with single-crystal X-ray diffraction.

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