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$(Mn_{1-x}Pb_x)Pb_{10+y}Sb_{12-y}S_{26-y}Cl_{4+y}O$, a new oxy-chloro-sulfide with ~2 nm-spaced $(Mn,Pb)Cl_4$ single chains within a waffle-type crystal structure

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Abstract

The new oxy-chloro-sulfide $(Mn_{1-x}Pb_x)Pb_{10+y}Sb_{12-y}S_{26-y}Cl_{4+y}O$ ($x \in [0.2–0.3]$; $y \in [0.3–1.6]$) was synthesized by dry way at 500–600 °C. A single crystal ~$Mn_{0.7}Pb_{11.0}Sb_{11.3}S_{25.3}Cl_{4.7}O$ indicates a monoclinic symmetry, space group $C2/m$, with $a = 37.480(8)$, $b = 4.1178(8)$, $c = 18.167(4)$ Å, $\beta = 106.37(3)°$, $V = 2690.2(9)$ Å^3, $Z = 2$. Its crystal structure was determined by X-ray single crystal diffraction, with a final $R = 5.11\%$. Modular analysis of the crystal structure reveals a "waffle" architecture, where complex rods with lozenge section delimitate an internal channel filled by a single chain of $(Mn_{0.7}Pb_{0.3})Cl_6$ octahedra connected by opposite edges. Minimal inter-chain distances are close to 18 Å. The rod wall, two-atom thick, presents, in alternation with S atoms, Pb or (Pb,Sb) cations with prismatic coordination in the internal atom layer, while the external atom layer is constituted exclusively by Sb cations with dissymmetric square pyramidal coordination. A $(Pb,Sb)_2S_2$ fragment connects two successive rods along (2 0 1) to form a waffle-type palissadic layer. The unique O position, half filled, presents the same environment than the isolated O positions in the oxy-sulfide $Pb_{14}Sb_{30}S_{54}O_5$, or oxy-chloro-sulfides $Pb_{18}Sb_{20}S_{46}Cl_2O$ and $(Cu,Ag)_2Pb_{21}Sb_{23}S_{55}ClO$. This compound belongs to a pseudo-homologous series of chalcogenides with waffle structure, ordered according to the size of their lozenge shape channel. Such a complex senary compound of the oxy-chloro-sulfide type illustrates the structural competition between three cations, on one hand, and, on the other hand, three anions. This compound is of special interest regarding the 1D distribution of magnetic Mn^{2+} atoms at the ~2 nm scale.

Keywords: Oxy-chloro-sulfide; Manganese; Lead; Antimony; Synthesis; Crystal structure; Homologous series

1. Introduction

Relatively to pure oxides, halogenides or chalcogenides, compounds associating two anions as specific independent constituents, like oxy-chalcogenides or halogeno-chalcogenides, are scarce. Nevertheless, such mixed anionic compounds are of great interest today, as they may often be described as composite structures, with anionic and cationic segregation in distinct building blocks, each one with its specific physical properties, as pointed by Cario [1]. Thus, one of the best example is that of LaCuOS [2], a transparent *p*-type semiconductor.

Reviews on halogeno-chalcogenides of transition elements were presented by different authors [3–5]. Various studies on quaternary compounds of the halogeno-chalcogenosalt type, associating one metal with one pnictogen, were performed recently : $LnSbS_2Br_2$ (Ln = La, Ce) [6,7], $MPnQ_2X$ family (M: Mn, Cd; Pn: Sb, Bi; Q: S, Se; X: Cl, Br, I) [8–12], $Cu_3Bi_2S_3I_3$ [13–15], $Cu_{6.2}PS_5Cl$ [15], Ag/Bi/(S,Se)/Cl compounds [15–18], $HgAs_4S_4I_2$ [19], Hg_3AsS_4Cl and Hg_3AsSe_4Cl [20], Pb_2AsS_3(I,Cl,Br) [21], Al/(Sb,Bi)/(S,Se,Te)/Cl [21–24].

A fortiori, more complex compounds of the oxy-halogeno-chalcogenide type, like synthetic $Eu_{27}Ti_{20}S_{54}X_2O_{12}$ ($X = I_{0.35}Cl_{0.65}$) [25] are rather uncommon. Recently, two compounds of the oxy-chloro-sulfosalt type were discovered as minerals, pillaite, $Pb_{18}Sb_{20}S_{46}Cl_2O$ [26], and pellouxite, $(Cu,Ag)_2Pb_{21}Sb_{23}S_{55}ClO$ [27]. Together with Pb and Sb as

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cations, sulfur constitutes the dominant anion, but the crystal structure studies [28,29] proved that minor chlorine and oxygen act as specific constituents. While pillaite is a quinary compound, pellouxite is a senary (or heptary) one, as there is also a single specific (Cu,Ag) position in the structure.

During the study of complex (Fe,Mn) chalcogenides and derivatives of the sulfosalt type with strong 1D magnetic properties [$MPb_4Sb_6S_{14}$, MSb_2S_4, $MPnQ_2X$ family (*M*: Mn, Fe; *Pn*: Sb, Bi; *Q*: S, Se; *X*: Cl, Br, I)] [10,30], a new oxy-chloro-sulfide with general composition $(Mn_{1-x}Pb_x)Pb_{10+y}Sb_{12-y}S_{26-y}Cl_{4+y}O$ (called hereafter "Mn-OClS") was obtained. In its crystal structure, the 1D organization of magnetic Mn^{2+} is strongly enhanced, with ~2 nm-spaced $(Mn,Pb)Cl_4$ chains. Its crystal chemistry is detailed here.

2. Experimental section

2.1. Synthesis

The studied compound "Mn-OClS" was first obtained (sample A) as a by-product by solid state reaction (ceramic) method from a mixture of FeS, $MnCl_2$, PbS and Sb_2S_3 in the 1/3/2/1 ratios, in order to obtain an ill-defined natural chloro-sulfosalt, $\sim(Mn_{1-x}Fe_x)_2PbSbS_3Cl_3$ [31,32]. Products were put under atmosphere into a silica tube and sealed under vacuum; the synthesis was performed at 500 °C during 10 days.

Single crystal study of rare fibres isolated from the bulk permitted to detect the new compound "Mn-OClS", and to determine its chemical composition, $\sim MnPb_{10}Sb_{12}S_{26}Cl_4O$. The weak oxygen content (0.34 wt.%) revealed by this study was apparently provided from oxidation traces within the reagents. On this basis, two new syntheses (B and C) were performed in a similar way without FeS, and with a starting composition close to the stoichiometric one given above (600 °C; MnS, $PbCl_2$, PbS and Sb_2S_3 — 1/2/10/5 and 1/2/8/6 ratios; 10 and 15 days respectively). A last attempt, performed adding oxygen as MnO (600 °C; MnO, $PbCl_2$, PbS and Sb_2S_3 — 1/2/8/6 ratios; 10 days), failed to obtain "Mn-OClS" (see Section 3.1). All final products were complex, fine grained mixtures of chloro- and oxy-chloro-sulfosalts of Pb and Sb, with or without minor Mn.

2.2. Chemical analysis

Chemical analyses of "Mn-OClS" and associated phases were performed on polished sections, first with a SEM equipped with an energy dispersive spectrometer (EDS). However, because of the overlapping of Pb, S and Cl emission lines using an EDS, and despite the use of a deconvolution program, there is a relatively high error on the measured weight concentration for these elements. Such a difficulty is ruled out through the analysis with electron probe microanalysis (EPMA) equipped with wavelength dispersive spectrometers (WDS). Only the analysis of oxygen is subject to uncertainty, due to its low concentration and to chemical artefacts. For instance, in scainiite, $Pb_{14}Sb_{30}S_{54}O_5$ [33,34] the oxygen content (theoretically 0.96 wt%) was clearly confirmed by EPMA. But when the measured oxygen content decreases down to 0.4 wt% or less, it may also be an artefact, due to the easy formation of an oxidation film at the polished surface of the sulfide. In this case, only the crystal structure study can prove the presence of oxygen, due to its localization on a specific atom position, as it will be shown for "Mn-OClS".

2.3. Crystallographic studies

Due to the chemical and crystallographic complexity of final products, X-ray powder diagrams were useless for the characterization of associated phases. Minute individual fibres were rarely observed, but only the first synthesis A provided fibres suitable for the X-ray single crystal study of "Mn-OClS". It crystallizes with monoclinic symmetry, space group *C*2/*m* (No. 12), with $a = 37.480(8)$, $b = 4.1178(8)$, $c = 18.167(4)$ Å, $\beta = 106.37(3)^\circ$, $V = 2690.2(9)$ Å^3, $Z = 2$. According to the specific position of the oxygen atom with a half site occupancy factor (s.o.f.), there must be a 2*b* superstructure, like in structures of related minerals pillaite, $Pb_{18}Sb_{20}S_{46}Cl_2O$ [28], pellouxite, $(Cu,Ag)_2Pb_{21}Sb_{23}S_{55}ClO$ [29] and scainiite, $Pb_{14}Sb_{30}S_{54}O_5$ [34]. Unfortunately, the quality of the studied crystal was not good enough to solve it. Table 1 gives the crystallographic data obtained on the studied fibre.

Table 1
Crystallographic Data for "Mn-OClS"

Chemical formula	$Mn_{0.72}Pb_{10.97}Sb_{11.31}S_{25.31}Cl_{4.69}O$
Formula weight (g mol^{-1})	4683.22
Crystal size (mm^3)	$0.008 \times 0.100 \times 0.010$
Crystal shape/colour	Needle/black
Temperature (K)	293(2)
Space group	*C*2/*m* (No. 12)
a (Å)	37.480(8)
b (Å)	4.1178(8)
c (Å)	18.167(4)
β (°)	106.37(3)
V (Å^3)	2690.2(9)
Z	2
μ (Mo-*K*α) (mm^{-1})	41.14
D_c (g cm^{-3})	5.782
No. unique reflns	4414
No. observed reflns ($I \geqslant 2\sigma(I)$)	2915
No. refined parameters	196
R_{int}	10.87%
Final R_1/wR ($I \geqslant 2\sigma(I)$)	5.11%/9.82%
GOF	1.018
Residual electronic density (e Å^{-3})	+2.83, −2.12

$R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$.

$wR = \left[\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2\right]^{1/2}$.