Synthesis of novel lead–molybdenum and lead–tungsten oxyhalides with the pinalite structure, $Pb_3MoO_5Cl_2$ and $Pb_3WO_5Br_2$

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ABSTRACT

Two new quaternary lead oxyhalides, $Pb_3MoO_5Cl_2$ and $Pb_3WO_5Br_2$, have been prepared. They are isostructural with the mineral pinalite, $Pb_3WO_5Cl_2$, and its barium analog. The crystal structure of $Pb_3MoO_5Cl_2$ has been refined from powder neutron diffraction data to $R_p = 0.0564$ and $R_{wp} = 0.0342$. All these structures contain significantly stretched MO_5 (M = Mo, W) square pyramids incorporated into the $[Pb_2O_2]$ sheets. Bond valence sums indicate significant overbonding of one of the metal sites, which increases along with structural distortions when passing from $Pb_3MoO_5Cl_2$ to $Pb_3WO_5Cl_2$ and from $Pb_3WO_5Cl_2$ to $Ba_3WO_5Cl_2$. Possibilities of preparing isostructural and structurally related compounds are discussed.

Keywords: $Pb_3MoO_5Cl_2$, pinalite, crystal structure, neutron diffraction

INTRODUCTION

Lead oxyhalide minerals are common phases that occur in oxidation zones of mineral deposits (Gillberg 1961; Dunn and Rouse 1985; Symes et al. 1994; Welch et al. 2000, etc.). The structures of natural and synthetic lead oxyhalides often exhibit fragments of tetragonal $[Pb_2O_2]$ layers observed in the structure of litharge, α-PbO (Krivovichev et al. 2004). In some oxygen-rich minerals and synthetic compounds, these layers remain as a whole and interleave with halide ion sheets. The interlayer charge balance is provided by two mechanisms, by either substitution of Pb^{2+} by higher-charged cations or diatomic groups, or by substitution of O^{2-} by a lower-charged anion (OH^-, F^-), or vacancy. These mechanisms can operate both separately, as in the case of perite $PbBiO_2Cl$ (Gillberg 1961) or the oxyfluoride analog of blixite Pb_2OFCl (Aurivillius 1977), and simultaneously, as in the case of thorikosite $Pb_3SbO_3(OH)Cl_2$ (Dunn and Rouse 1985) and freedite $Pb_8As_2O_9\square CuCl_5$ (Pertlik 1987; $\square$ = oxygen vacancy). All these structures originate from two archetypic subcells corresponding to ideal M_2O_2X and M_4O_4X compositions (Fig. 1), and ordering of cations, anions, and/or vacancies result in various superstructures (see Cooper et al, 1994; Welch et al. 1996, 2000, 2001; Welch 2004, as well as references therein).

The substitution of Pb^{2+} by diatomic metal-oxygen groups is common only among oxyhalides of this particular element though it has been once observed for $[M_2L_2]$ layers of other compositions. Most known examples are derived from the structure shown in Figure 1b, the "extra" O atoms protruding into the interlayer space akin to the $Pb_{1-x}(TiO)_xO$ solid solution (Garnier et al. 1990; Cooper et al. 1994; Welch et al. 1996). In the M_2O_2X structure (Fig. 1a), there is very little free space for the

"extra" oxygen, the only two known examples being pinalite, $Pb_3(WO)O_4Cl_2$ (Dunn and Grice 2000, Fig. 2a), and its barium analog, $Ba_3WO_5Cl_2$ (Spitsyn et al. 1985). The "extra" oxygen of the WO^{4+} group is projected into the $[Cl^-]$ layer pushing the chlorine atoms aside and leaving almost no room for the lone pair of the neighboring lead atom. A related structure of $Ca_3WO_5Cl_2$ (Zikmund 1974) (Fig. 2b) corresponds to different ordering of Ca^{2+} and WO^{4+} and displays particularly significant displacement of chlorine atoms from their ideal positions. This causes essential strain, and it is of interest whether any isostructural or structurally related analogs containing molybdenum and other halogens can exist.

Formation of a compound $Pb_3MoO_5Cl_2$ was detected during an attempt to grow single crystals of Pb_2MoO_5 from $PbCl_2$ flux (Bazarova et al. 1980). However, the observed X-ray pattern was not indexed. As yet, nothing is known about compounds of other halogens. In the current paper, we report the results of our attempts to prepare possible analogs of pinalite among oxyhalides of lead.

EXPERIMENTAL METHODS

The starting compounds were yellow PbO, MoO_3, WO_3, and lead halogenides. The synthetic conditions were the same as in Bazarova et al. 1980. First, Pb_2MoO_5 and $PbWO_4$ were prepared at 700 °C for 120 h, with one intermediate grinding. Mixtures of Pb_2MoO_5 + PbX_2 or $PbWO_4$ + PbO + PbX_2 were thoroughly ground and annealed in evacuated silica capsules at 400 °C for 12 h, reground and annealed again at 500 °C (X = Cl, Br) or 400 °C (X = I) for another 12 h. It was soon found that $Pb_3MoO_5Cl_2$ can also be prepared in covered alumina crucibles in air under the same thermal treatment.

X-ray diffraction patterns were recorded in a Guinier camera FR-552, En-raf-Nonius, and interpreted using a local program and semiconductor quality germanium as an internal standard. Two new compounds isostructural to pinalite, $Pb_3MoO_5Cl_2$ and $Pb_3WO_5Br_2$ were found and their diffraction patterns indexed by analogy with orthorhombic cell parameters, $a = 11.034(3)$ Å, $b = 13.056(5)$ Å, $c = 5.599(2)$ Å for $Pb_3MoO_5Cl_2$ and $a = 11.217(3)$ Å, $b = 13.323(3)$ Å, $c = 5.677(2)$ Å for $Pb_3WO_5Br_2$. In other cases, mixtures of $PbMO_4$ (M = Mo, W) and unknown compounds were obtained. The mixture of Pb_2MoO_5 and PbI_2 turned black upon
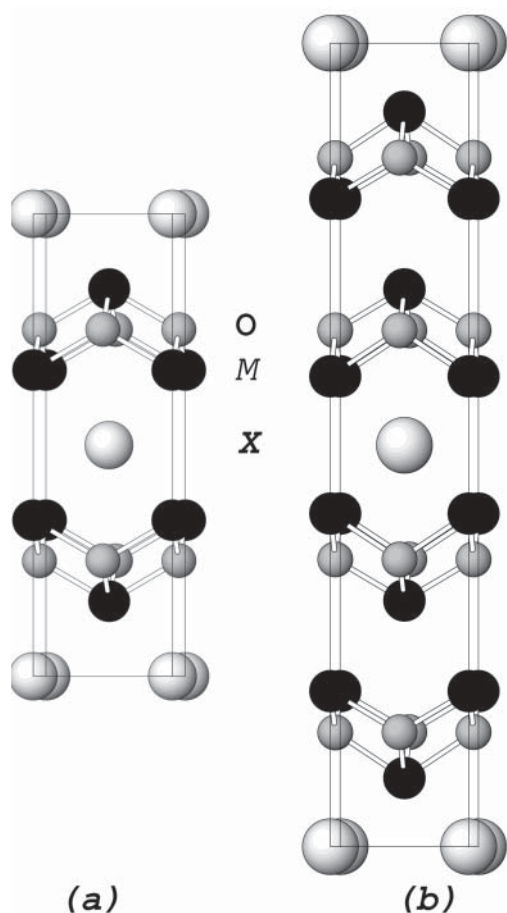
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FIGURE 1. Tetragonal subcells of lead oxyhalides: (**a**) M_2O_2X, (**b**) M_4O_4X.

FIGURE 2. Final Rietveld refinement plot for the $2\theta = 145\ °C$ data set.

TABLE 1. Conditions of powder diffraction experiment for $Pb_3MoO_5Cl_2$

	Histogram 1 (90°)	Histogram 2 (145°)
Crystal system	Orthorhombic	
Space group	*Amam* (#63)	
Cell parameters (errors):		
a (Å)	11.0116(1)	
b (Å)	13.1149(2)	
c (Å)	5.59485(5)	
V (Å³)	807.98(1)	
Z	4	
Calculated density (g/cm³)	7.139	
Analyzing package	GSAS	
d range (Å)	0.44–4.2	0.5–3.2
Number of free parameters	36	
Number of data points	4524	3697
Number of reflections	3276	2035
R_p, R_{wp}	0.0462, 0.0249	0.0544, 0.0217
R_p, R_{wp} (excluding background)	0.0496, 0.0334	0.0695, 0.0348
R (F^2)	0.0651	0.0615
Overall parameters:		
R_p, R_{wp}	0.0489, 0.0228	
R_p, R_{wp} (excluding background)	0.0564, 0.0342	
χ^2	2.90	

TABLE 2. Atomic parameters and calculated bond valence sums for $Pb_3MoO_5Cl_2$ [*Amam*, $a = 11.0116(1)$ Å, $b = 13.1149(2)$ Å, $c = 5.59485(5)$ Å]

Atom	Wyckoff site	x	y	z	U_{iso}	BVS
Pb1	8f	0.46809(7)	0.34936(6)	0	0.0088(2)	2.05
Pb2	4c	0.75	0.39734(9)	0.5	0.0105(2)	2.33
Mo	4c	0.75	0.2345(1)	0	0.0056(2)	6.03
O1	16h	0.63002(8)	0.27023(7)	0.2327(1)	0.0066(1)	2.10
O2	4c	0.75	0.1045(2)	0	0.0159(4)	1.93
Cl1	4a	0.5	0.5	0.5	0.0222(3)	0.81
Cl2	4c	0.75	0.4763(1)	0	0.0143(3)	1.04

TABLE 3. Calculated bond distances (in Å) for $Pb_3MoO_5Cl_2$, $Pb_3WO_5Cl_2$, and $Ba_3WO_5Cl_2$

Bond	$Pb_3MoO_5Cl_2$	$Pb_3WO_5Cl_2$	$Ba_3WO_5Cl_2$
A1–O1 (×2)	2.422(1)	2.429(14)	2.614(2)
A1–O1 (×2)	2.439(1)	2.463(13)	2.617(2)
A1–Cl1 (×2)	3.443(1)	3.452(1)	3.617(1)
A1–Cl2 (×1)	3.316(1)	3.333(9)	3.208(5)
A1–Cl2 (×1)	3.522(1)	3.533(6)	3.940(5)
A2–O1 (×4)	2.600(1)	2.621(14)	2.712(1)
A2–O2 (×1)	2.718(2)	2.676(52)	2.914(3)
A2–Cl1 (×2)	3.065(1)	3.060(1)	3.136(1)
A2–Cl2 (×2)	2.983(1)	2.974(4)	3.135(1)
M–O1 (×4)	1.913(1)	1.901(14)	1.904(7)
M–O2 (×1)	1.704(3)	1.699(52)	1.752(30)
M–Cl2 (×4)	3.172(2)	3.136(13)	3.442(1)

annealing, which indicates a possible redox reaction. Both oxyhalides decompose above 500 °C.

All attempts to grow single crystals of $Pb_3MoO_5Cl_2$ from $PbCl_2$ or $CsCl-PbCl_2$ fluxes were unsuccessful. It was also found that the X-ray pattern of $Pb_3MoO_5Cl_2$ changed significantly after the sample came in contact with liquid water even for several minutes. Because a 10 g batch of single-phase $Pb_3MoO_5Cl_2$, as opposed to $Pb_3WO_5Br_2$, could be easily prepared, the oxychloride was chosen for structure determination from neutron powder diffraction data.

STRUCTURE DETERMINATION

Neutron powder diffraction data were collected on the high flux diffractometer POLARIS (at 25 °C) at the ISIS facility (Rutherford Lab, Chilton, U.K.) that operates in energy-dispersive (time-of-flight) mode. Approximately 10 g of the sample was placed in a cylindrical vanadium can and data were collected for 1 h. The data from both 145°and 90°detector banks were used for Rietveld analysis employing the GSAS package (von Dreele and Larson 1987).

The starting model was the structure of $Pb_3WO_5Cl_2$ (Dunn and Grice 2000). The solution converged rapidly to quite low R values (Table 1). The final Rietveld refinement plot for the $2\theta = 145°$ data set is given in Figure 3. The atomic coordinates are listed in Table 2. Generated bond distances, together with reference data for $Pb_3WO_5Cl_2$ and $Ba_3WO_5Cl_2$, are presented in Table 3. We note that the precision of this structure, determined from neutron powder diffraction, is markedly better than that of $Pb_3WO_5Cl_2$, determined by single-crystal X-ray diffraction (e.g., a factor of 10 improvement in precision for Pb-O and particularly Mo-O bond lengths). This is not surprising due to heavy absorption of X-rays almost exclusively by lead atoms while in neutron diffraction, differences in scattering power of contributing atoms are less pronounced.
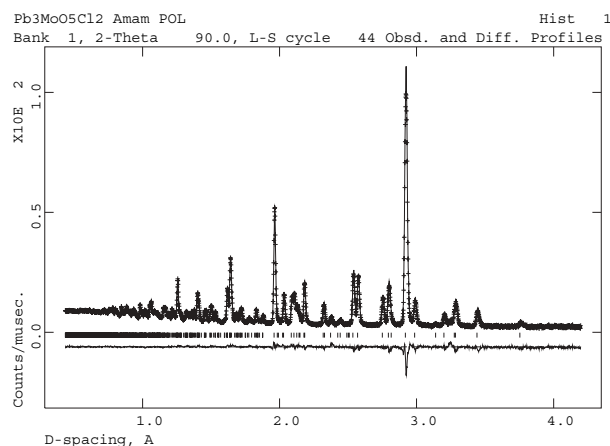
FIGURE 3. Crystal structures of (**a**) $Pb_3WO_5Cl_2$, (**b**) $Ca_3WO_5Cl_2$. Ca/Pb = dark gray spheres; O = small light spheres; Cl = large light spheres. The WO_5 square pyramids are shown.

RESULTS AND DISCUSSION

Our investigations have added two new representatives to the structure type of pinalite. However, only three of the six possible $Pb_3MO_5X_2$ oxyhalides (M = Mo, W; X = Cl, Br, I) actually exist. This can be explained considering the strain induced by the intrusion of the "extra" oxygen into the relatively dense M_2O_2X structure. This results in displacement of the halide ions aside from the oxygen, causing concomitant displacements of lead and, finally, oxygen atoms of the $[Pb_2O_2]$ layer away from the transition metal ion. The data given in Table 3 show that the Pb2-Cl bonds are significantly shortened relative to the Pb1-Cl bonds and, additionally, a further bond is formed (Pb2-O2). Bond-valence analysis, performed by the program VaList (Brown and Wills 1999) using parameters from Altermatt and Brown (1985) and Brese and O'Keeffe (1991) reveals that the Pb2 site is seriously overbonded. In fact, the Pb2 bond valence sum calculated by Dunn and Grice (2000) is in error. The true bond valence sums for Pb2 are 2.31 for $Pb_3WO_5Cl_2$ and 2.32 for $Pb_3MoO_5Cl_2$, both being significantly above the optimum value of 2 valence units.

These values might be expected to further increase when proceeding to structures containing larger Br⁻ and I⁻ anions, and it is possible that the strain in the hypothetical structure of $Pb_3MoO_5Br_2$ exceeds the stability limit of the Pb2 site. Oxyiodides are formed for neither Mo nor W. Replacement of Pb^{2+} by larger Ba^{2+} also increases the overbonding of the M2 site, and it is not yet clear if other alkaline earth analogs can exist. Our preliminary results indicate existence of $Ba_3MoO_5Cl_2$ isostructural to $Ba_3WO_5Cl_2$ [$a = 11.400(3)$ Å, $b = 13.919(4)$ Å, and $c = 5.766(1)$ Å], but this compound is very unstable and could not as of yet be prepared in pure form. Attempts to prepare oxybromides and

strontium analogs have so far been unsuccessful. An alternative is the structure of $Ca_3WO_5Cl_2$ where the square-pyramidal WO_5^{2-} geometry is retained, but the coordination number around the Ca^{2+} ions is greatly reduced, to either 5 or 6.

These distortions should disappear or significantly decrease when proceeding to the structure shown in Figure 1b where there is enough free space for the extra oxygen in the interlayer space. A model for the structure of another lead-molybdenum oxychloride, $Pb_7MoO_9Cl_2$, has been proposed by Welch (1996). This compound is stable enough to occur as a natural mineral parkinsonite (Symes et al. 1994). In fact, all $Pb_7MO_9X_2$ (M = Mo, W, and X = Cl, Br, I) parkinsonite analogs have been prepared except $Pb_7MoO_9I_2$ (Aurivillius 1982). The latter is not surprising as Mo^{VI} seems to be reducible by I⁻.

Another way to partially decrease the strain in the $Pb_{2-x}(MO)_xO_2X$ structure is to replace MoO^{4+} with higher-charged ReO^{5+}, which would reduce x down to $^1/_3$ compared to $^1/_2$ for $Pb_{1.5}(MoO)_{0.5}O_2X$ ($\equiv Pb_3MoO_5X_2$). Attempts have been made to prepare the corresponding $Pb_{1.67}(ReO)_{0.33}O_2X$ ($\equiv Pb_5ReO_7X_3$) oxyhalides (X = Cl, Br, I) from $Pb_3O_2X_2$ and $PbRe_2O_8$; X-ray patterns indicated formation of all three target compounds but contained broad lines from which only tetragonal subcell parameters could be estimated. The situation resembles that of schwartzembergite $Pb_5IO_4(OH)_2Cl_3$ (Welch et al. 2001) with the same lead:heteroatom ratio, where only tetragonal substructure could be refined using X-ray diffraction. Despite their preliminary nature, our results on $Pb_5ReO_7X_3$ (X = Cl, Br, and I) clearly indicate the possibility of obtaining even oxyiodides by lowering the content of "extra" O atoms in the $M_2O_{2+x}X$ structure. Structural details of the rhenium compounds will be the topic of a separate communication.

As yet, the mechanism of substituting an atom in the $[M_2L_2]$

layers by a diatomic group seems to operate easily only in case of lead (and, possibly, alkaline earth) oxyhalides. Even partial substitution of Pb^{2+} by some ions close in size or electron configuration in the pinalite structure seems to be sufficiently hindered. Though the strain would be evidently reduced by substituting the nine-coordinated $(Pb2)^{2+}$ by Sr^{2+}, which has a similar radius but no lone pair, $Pb_2SrMoO_5Cl_2$ could not be prepared. It is possible that size effects also play an essential role, i.e., while $Ba_3WO_5Cl_2$ is a complete analog of $Pb_3WO_5Cl_2$, $Ca_3WO_5Cl_2$ has a different structure. All attempts to synthesize $Pb_2BiNbO_5Cl_2$, $Bi_3NbO_5Se_2$, or $Bi_3FeO_5Cl_2$ have been unsuccessful.

In conclusion, we were able to prepare Mo and Br analogs of pinalite. Whereas the natural occurence of $Pb_3WO_5Br_2$ is unlikely, Mo-bearing pinalite $Pb_3MoO_5Cl_2$ may be a stable phase in oxidation zones of Pb mineral deposits.

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