Synthesis of novel lead–molybdenum and lead–tungsten oxyhalides with the pinalite structure, Pb$_3$MoO$_5$Cl$_2$ and Pb$_3$WO$_5$Br$_2$

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ABSTRACT

Two new quaternary lead oxyhalides, Pb$_3$MoO$_5$Cl$_2$ and Pb$_3$WO$_5$Br$_2$, have been prepared. They are isostructural with the mineral pinalite, Pb$_5$WO$_4$Cl$_2$, and its barium analog. The crystal structure of Pb$_3$MoO$_5$Cl$_2$ has been refined from powder neutron diffraction data to $R_p = 0.0564$ and $R_w = 0.0342$. All these structures contain significantly stretched MO$_5$ (M = Mo, W) square pyramids incorporated into the [Pb$_2$O$_2$] sheets. Bond valence sums indicate significant overbonding of one of the metal sites, which increases along with structural distortions when passing from Pb$_5$MoO$_4$Cl$_2$ to Pb$_5$WO$_4$Cl$_2$ and from Pb$_5$WO$_4$Cl$_2$ to Ba$_3$WO$_5$Cl$_2$. Possibilities of preparing isostructural and structurally related compounds are discussed.

Keywords: Pb$_3$MoO$_5$Cl$_2$, 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$_2$O$_2$] 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 vacuum. These mechanisms can operate both separately, as in the case of perite PbBiO$_2$Cl (Gillberg 1961) or the oxyfluoride analog of blixite Pb$_4$OFCl$_2$ (Aurivillius 1977), and simultaneously, as in the case of thorikosite Pb$_2$SbO$_4$(OH)Cl$_2$ (Dunn and Rouse 1985) and freedite Pb$_5$As$_2$O$_4$I$_2$CuCl$_2$ (Pertlik 1987; $\Box$ = oxygen vacancy). All these structures originate from two archetypic subcells corresponding to ideal M$_2$O$_2$X and M$_4$O$_4$X 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$_2$L$_2$] 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$_2$(TiO)$_2$O solid solution (Garnier et al. 1990; Cooper et al. 1994; Welch et al. 1996). In the M$_2$O$_2$X structure (Fig. 1a), there is very little free space for the “extra” oxygen, the only two known examples being pinalite, Pb$_5$(WO$_4$)Cl$_2$ (Dunn and Grice 2000, Fig. 2a), and its barium analog, Ba$_5$WO$_4$Cl$_2$ (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$_5$WO$_4$Cl$_2$ (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$_5$MoO$_4$Cl$_2$ was detected during an attempt to grow single crystals of Pb$_3$MoO$_5$ 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$_3$MoO$_5$ and PbWO$_4$ were prepared at 700 °C for 120 h, with one intermediate grinding. Mixtures of Pb$_2$MoO$_4$ + 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$_3$MoO$_4$Cl$_2$ 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, Enraf-Nonius, and interpreted using a local program and semiconductor quality germanium as an internal standard. Two new compounds isostructural to pinalite, Pb$_3$MoO$_5$Cl$_2$ and Pb$_3$WO$_5$Br$_2$, 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$_3$MoO$_5$Cl$_2$ and $a = 11.217(3)$ Å, $b = 13.323(3)$ Å, $c = 5.677(2)$ Å for Pb$_3$WO$_5$Br$_2$. In other cases, mixtures of Pb$_3$MO$_4$ (M = Mo, W) and unknown compounds were obtained. The mixture of Pb$_3$MoO$_5$ and PbI$_2$ turned black upon