Symesite, \(\text{Pb}_{10}(\text{SO}_4)\text{O}_7\text{Cl}_4(\text{H}_2\text{O})\), a new PbO-related sheet mineral: Description and crystal structure

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ABSTRACT

Symesite, \(\text{Pb}_{10}(\text{SO}_4)\text{O}_7\text{Cl}_4(\text{H}_2\text{O})\), is a Pb sheet mineral found in the oxidized zone of a Carboniferous Mn-Pb-Cu deposit at Merehead Quarry, Somerset. It occurs as pink crystal blebs up to 2 mm long and as pink crystalline aggregates up to 1 cm in diameter, and is associated with serussite, hydrocerussite, paralaurionite, blixite, chloroxiphite, pyrolusite, coronadite, hematite, parkinsonite, and mereheadite. Crystals of symesite are blocky, translucent pink with a vitreous luster and a white streak. Mohs hardness is 4, \(D_{\text{meas}} = 7.3(2) \text{g/cm}^3\) and there is a perfect cleavage parallel to \(\{001\}\); the refractive indices exceed 2. Electron-microprobe analysis gave the following composition (wt%): \(\text{Pb} 90.66, \text{SO}_3 3.15, \text{Cl} 5.83 (O = \text{Cl} 1.32)\), sum 98.32, giving the anhydrous formula \(\text{Pb}_{10.31} \text{S}_{1.00} \text{O}_{11.22} \text{Cl}_{4.18}\); solution of the crystal structure gave the ideal formula \(\text{Pb}_{10}(\text{SO}_4)\text{O}_7\text{Cl}_4(\text{H}_2\text{O})\). The six strongest peaks in the X-ray powder-diffraction pattern \([d \text{ in Å}, (hkl)]\) are: 2.911 (10)(414, 323), 3.286 (9)(004), 2.955 (9)(412), 2.793 (8)(71–1, 131), 6.573 (4)(002), 3.768 (4)(412, 321). The structure of symesite was solved by direct methods and refined to an \(R\) index of 4.0%. Symesite is triclinic, space group \(\text{B}1\), \(a = 19.727(2), b = 8.796(1), c = 13.631(2) \text{Å}, \alpha = 82.21(1), \beta = 78.08(1), \gamma = 100.04(1)\)\(^\circ\), \(V = 2242.4(5) \text{Å}^3\), \(Z = 4\). The structural unit of symesite is a \([\text{Pb}_{10}(\text{SO}_4)\text{O}_7]\)\(^{4+}\) single sheet; adjacent sheets are linked by layers of Cl. One-eleventh of the Pb atoms are replaced by S, with the addition of an apical oxygen to form an \(\text{SO}_4\) tetrahedron and a compensating O vacancy within the PbO sheet. The distribution of Pb and \(\text{SO}_4\) groups is highly ordered and defines a 22 cation-site superstructure motif within the PbO sheet. Eight of eleven interlayer anion sites are occupied by Cl, two are occupied by O of \(\text{H}_2\text{O}\) groups, and one site is vacant. Incident bond-valence sums at O atoms indicate that hydrogen bonds occur between the \(\text{H}_2\text{O}\) group and the apical oxygen of the \(\text{SO}_4\) group, providing additional linkage between adjacent PbO sheets. The structure of symesite is closely related to those of tetragonal PbO and the family of PbO-related sheet minerals that includes nadorite, thorikosite, mereheadite, parkinsonite, and kombatite. There are ten non-equivalent Pb sites with coordination numbers of five, seven, or eight; these polyhedra are variants of the \(\text{Pb}[\text{O}_4\text{Cl}_4]\) square-antiprism that is characteristic of these minerals.

INTRODUCTION

The PbO-related oxychlorides have sheet structures in which litharge-like sheets and layers of Cl are intercalated. What makes them particularly interesting from a crystal-chemical point of view is the diverse range of elements that substitute into these structures: As, Sb, V, Mo, W, P, Si, and I. Charge balance is provided by Cl which forms layers between the PbO-like sheets. Almost all structural studies of these oxychlorides have used single-crystal X-ray diffraction and have defined two types of substructure, related topologically to tetragonal PbO (litharge) or orthorhombic PbO (massicot). The (sub) structures obtained in these studies imply that the distribution of Pb and the substituent group within the PbO layers is disordered. However, a study of parkinsonite by electron diffraction (Welch et al. 1996) revealed weak but sharp superstructure reflections arising from ordering of Pb and Mo, in this case as \(\text{Pb}_3\text{Mo}\) and \(\text{Pb}_7\text{Mo}\) motifs. The superstructure reflections were missed in most previous XRD studies, possibly because of the high X-ray absorption coefficients of these minerals. In contrast, the very thin crystallites observed by electron diffraction (TEM) transmit electrons sufficiently well to allow superstructure reflections to be recorded in 1–2 min exposures. The relations between the substructure and superstructure were deduced from the electron-diffraction patterns in which the substructure reflections are much more intense than the superstructure reflections. In comparison, an eight-day exposure was needed to record very faint superstructure reflections by X-ray precession photography. For symesite, the TEM observations suggest that, far from being disordered, Pb and S are highly ordered within the PbO layers. The only X-ray study to date that has recognized a superstructure is that of Cooper and Hawthorne (1994) for kombatite, \(\text{Pb}_{14}(\text{VO}_4)\text{O}_9\text{Cl}_4\).

Symesite is a hydrated Pb-S-oxychloride, \(\text{Pb}_{10}(\text{SO}_4)\text{O}_7\text{Cl}_4(\text{H}_2\text{O})\), and a new member of the nadorite family of Pb-sheet minerals. The mineral and name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. It is named for Robert Symes (1937–) of the Department of Mineralogy, the Natural History Museum (London), in recognition of his many contri-