Roeblingite, Pb$_2$Ca$_6$(SO$_4$)$_2$(OH)$_2$(H$_2$O)$_4$[Mn(Si$_3$O$_9$)$_2$]: its crystal structure and comments on the lone pair effect

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Abstract

Roeblingite, Pb$_2$Ca$_6$(SO$_4$)$_2$(OH)$_2$(H$_2$O)$_4$[Mn(Si$_3$O$_9$)$_2$], monoclinic holosymmetric, $a = 13.208(4)$, $b = 8.287(2)$, $c = 13.089(9)$Å, $\beta = 106.65(6)^\circ$, space group $C2/m$, possesses a \( \frac{1}{2} \)Mn(Si$_3$O$_9$)$_2$\( \upsilon \) corner-linked sheet oriented parallel to \( c \)\{001\}, the plane of perfect micaceous cleavage. $R = 0.066$ for 2479 nonequivalent reflections.

The large cations are tucked between the [Mn(Si$_3$O$_9$)$_2$] sheets. All vertices of the MnO$_6$ octahedron link to the (Si$_3$O$_9$) radicals which are oligosilicate three-membered rings and are geometrically similar to the rings in paragenetically related margarosanite, PbCa$_3$[Si$_5$O$_{14}$]. Coordination polyhedra include Pb$_9$ (maximal point symmetry mm2); Ca(1)\( \phi \) distorted square antiprisms; Ca(2)\( \phi \) polyhedra similar to Pb\( \phi \); MnO$_6$ octahedra: SiO$_4$, SO$_4$ tetrahedra. Mean bond distances are: Pb-O 2.82 (2.22 to 3.42), Ca(1)O 2.53, Ca(2)O 2.43, Mn-O 2.22, Si(1)O 1.64, Si(2)O 1.62 and S-O 1.47Å.

The packing efficiency, defined as the volume of the unit cell divided by the total number of anions in that cell, is usually close to the values of hcp or cph oxyxalts structures for most minerals which don’t have channels. This value, $V_{E}$, is unusually large for Pb(II) oxyxalts. By including the number of lone pair cations for that cell, the value, $V_{E+L}$ is more reasonable and approximates the packing efficiencies for oxyxalts with those cations of similar size but stripped of all valence electrons.

Introduction

Roeblingite is an exotic phase, presently known from two localities. It was described from the type locality at Franklin, New Jersey (Penfield and Foote, 1897) as a sulfite-bearing silicate; Blix (1931) showed that it is a sulfate-bearing silicate, based on the Franklin material and a more recent find from Långban, Sweden where it occurred as fracture fillings. Foit (1966) examined its crystallographic character on coarse platy Långban material. We agree with his findings, except that the space group appears to be C2/m, not C2/c. Finally, Dunn et al. (1982) reported several new chemical analyses on roebelingite, but the differences from the Blix analysis are small. We include their chemical analysis for a Långban roebelingite in Table 1.

The senior author has long been interested in roebelingite; over fifteen years ago, crystals were secured from the Swedish Natural History Museum with plans of eventually unravelling its structure, and especially determining the role of the sulfur cation. More recently, increased interest in Pb(II) from oxyxalts and sulfosalt environments and the micaceous nature of the material prompted a more detailed structure investigation.

Experimental procedure

At least ten chemical analyses have been reported in the literature, and three are selected for Table 1. One of the motivations for the present study concerns the formal charge on sulfur: is it S$^+$ or S$^{2-}$? Penfield and Foote (1897) were cautious in their study and reported SO$_3$ as the oxide. However, Blix (1931) re-invigated the problem, analyzing Franklin material and the recent find of Långban material. He concluded that sulfur occurred as SO$_3$, a conclusion we similarly make on the basis of structure study, for Långban material at least.

A small vial of palest pink flakes from Långban,
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