

Table with 21 columns: h, k, l, Fo, Fc, s (repeated 3 times). Each row contains numerical values for these parameters, representing observed and calculated structure factors for Sidpietersite in P-1.

| h | k | l | Fo | Fc | s | h | k | l | Fo | Fc | s | h | k | l | Fo | Fc | s | h | k | l | Fo | Fc | s | h | k | l | Fo | Fc | s |
|----|----|----|-----|------|-----|----|----|----|-----|------|-----|----|----|----|----|-----|-----|----|----|----|-----|------|-----|----|----|----|-----|-----|-----|
| -1 | -4 | 11 | 39 | -32 | 6 | -1 | -8 | 12 | 16 | -22 | -16 | -6 | -2 | 12 | 85 | 82 | 4 | 1 | -7 | 13 | 23 | -17 | -12 | -2 | 1 | 13 | 66 | -70 | 5 |
| 0 | -4 | 11 | 137 | 129 | 3 | 0 | -8 | 12 | 10 | 20 | -10 | -5 | -2 | 12 | 22 | 15 | -15 | 2 | -7 | 13 | 34 | 32 | -8 | -1 | 1 | 13 | 43 | -45 | 6 |
| 1 | -4 | 11 | 105 | 100 | 3 | 1 | -8 | 12 | 34 | 27 | -7 | -6 | -1 | 12 | 74 | -77 | 4 | 3 | -7 | 13 | 62 | 57 | 5 | 0 | 1 | 13 | 11 | -13 | -11 |
| 2 | -4 | 11 | 37 | -36 | 6 | 2 | -8 | 12 | 33 | -37 | -8 | -5 | -1 | 12 | 34 | -34 | -8 | -4 | -6 | 13 | 51 | 48 | 6 | 1 | 1 | 13 | 11 | 8 | -11 |
| 3 | -4 | 11 | 50 | 49 | 5 | -4 | -7 | 12 | 10 | -11 | -10 | -4 | -1 | 12 | 10 | 11 | -10 | -3 | -6 | 13 | 53 | 47 | 6 | 2 | 1 | 13 | 47 | 50 | 6 |
| 4 | -4 | 11 | 86 | -85 | 3 | -3 | -7 | 12 | 19 | 7 | -19 | -3 | -1 | 12 | 10 | -1 | -10 | -2 | -6 | 13 | 17 | -12 | -17 | 3 | 1 | 13 | 40 | 36 | 6 |
| 5 | -4 | 11 | 59 | -61 | 5 | -2 | -7 | 12 | 10 | -3 | -10 | -2 | -1 | 12 | 78 | 80 | 3 | -1 | -6 | 13 | 35 | 28 | -8 | -1 | -7 | 14 | 56 | -52 | 5 |
| 6 | -4 | 11 | 22 | 17 | -16 | -1 | -7 | 12 | 10 | -15 | -10 | -1 | -1 | 12 | 49 | 48 | 5 | 0 | -6 | 13 | 44 | -39 | 6 | 0 | -7 | 14 | 63 | 63 | 5 |
| 7 | -4 | 11 | 40 | -38 | 7 | 0 | -7 | 12 | 32 | 24 | -7 | 0 | -1 | 12 | 25 | 12 | -10 | 1 | -6 | 13 | 38 | -37 | 7 | 1 | -7 | 14 | 82 | 80 | 4 |
| -7 | -2 | 11 | 25 | -34 | -13 | 1 | -7 | 12 | 10 | 14 | -10 | -5 | 0 | 12 | 20 | -18 | -20 | 2 | -6 | 13 | 10 | 14 | -10 | -1 | -6 | 14 | 53 | -54 | 6 |
| -6 | -2 | 11 | 26 | -22 | -11 | 2 | -7 | 12 | 10 | -1 | -10 | -4 | 0 | 12 | 18 | -31 | -18 | 3 | -6 | 13 | 11 | -22 | -11 | 0 | -6 | 14 | 20 | -26 | -20 |
| -6 | -1 | 11 | 41 | 45 | 7 | 3 | -7 | 12 | 10 | 8 | -10 | -3 | 0 | 12 | 51 | -52 | 5 | 4 | -6 | 13 | 16 | 20 | -16 | 1 | -6 | 14 | 89 | -84 | 4 |
| -5 | -1 | 11 | 48 | -48 | 5 | 4 | -7 | 12 | 34 | -32 | -8 | -2 | 0 | 12 | 17 | -20 | -17 | 2 | -5 | 13 | 27 | 24 | -11 | 2 | -6 | 14 | 61 | 54 | 5 |
| -4 | -1 | 11 | 32 | 36 | -7 | -5 | -6 | 12 | 27 | 27 | -12 | -1 | 0 | 12 | 10 | 16 | -10 | 3 | -5 | 13 | 21 | 13 | -21 | 3 | -6 | 14 | 35 | 35 | -9 |
| -3 | -1 | 11 | 39 | 31 | 6 | -4 | -6 | 12 | 46 | -39 | 6 | 0 | 0 | 12 | 16 | 3 | -16 | 4 | -5 | 13 | 11 | 22 | -11 | -4 | -2 | 14 | 41 | -37 | 7 |
| -2 | -1 | 11 | 78 | -81 | 3 | -3 | -6 | 12 | 10 | 4 | -10 | 1 | 0 | 12 | 39 | 39 | 5 | 5 | -5 | 13 | 19 | 19 | -19 | -3 | -2 | 14 | 22 | 21 | -16 |
| -3 | 0 | 11 | 57 | -61 | 4 | -2 | -6 | 12 | 41 | -42 | 6 | 2 | 0 | 12 | 10 | 5 | -10 | -5 | -2 | 13 | 44 | 41 | 6 | -2 | -2 | 14 | 17 | 9 | -17 |
| -2 | 0 | 11 | 114 | 117 | 3 | -1 | -6 | 12 | 56 | -54 | 4 | 3 | 0 | 12 | 17 | -17 | -17 | -4 | -2 | 13 | 50 | -46 | 6 | -3 | -1 | 14 | 44 | 39 | 6 |
| -1 | 0 | 11 | 46 | 49 | 5 | 0 | -6 | 12 | 48 | 44 | 5 | 4 | 0 | 12 | 35 | 23 | -8 | -5 | -1 | 13 | 50 | -47 | 5 | -2 | -1 | 14 | 84 | -83 | 4 |
| 0 | 0 | 11 | 68 | -63 | 4 | 1 | -6 | 12 | 10 | -4 | -10 | 5 | 0 | 12 | 11 | -14 | -11 | -4 | -1 | 13 | 117 | 115 | 3 | -1 | -1 | 14 | 32 | 29 | -8 |
| 1 | 0 | 11 | 69 | 68 | 4 | 2 | -6 | 12 | 55 | 52 | 4 | -2 | 1 | 12 | 65 | 61 | 5 | -3 | -1 | 13 | 51 | 47 | 5 | 0 | -1 | 14 | 57 | -58 | 5 |
| 2 | 0 | 11 | 137 | -134 | 3 | 3 | -6 | 12 | 80 | 72 | 3 | -1 | 1 | 12 | 47 | -47 | 5 | -2 | -1 | 13 | 51 | 51 | 5 | 1 | -1 | 14 | 59 | -61 | 5 |
| 3 | 0 | 11 | 67 | -70 | 4 | 4 | -6 | 12 | 27 | -28 | -10 | 0 | 1 | 12 | 18 | 22 | -18 | -1 | -1 | 13 | 70 | 71 | 4 | 2 | -1 | 14 | 67 | 66 | 5 |
| -1 | 1 | 11 | 51 | -54 | 5 | 5 | -6 | 12 | 23 | 16 | -14 | 1 | 1 | 12 | 24 | 24 | -12 | 0 | -1 | 13 | 124 | -114 | 3 | 3 | -1 | 14 | 37 | -31 | -7 |
| 0 | 1 | 11 | 152 | 146 | 3 | -3 | -5 | 12 | 76 | 72 | 4 | 2 | 1 | 12 | 70 | -70 | 4 | 1 | -1 | 13 | 51 | -51 | 5 | 4 | -1 | 14 | 68 | 62 | 5 |
| 1 | 1 | 11 | 44 | 48 | 5 | -2 | -5 | 12 | 65 | -62 | 4 | 3 | 1 | 12 | 40 | 35 | 6 | 2 | -1 | 13 | 71 | -65 | 4 | -2 | 0 | 14 | 91 | 89 | 4 |
| 2 | 1 | 11 | 26 | 33 | -10 | -1 | -5 | 12 | 45 | 50 | 5 | 4 | 1 | 12 | 30 | -37 | -9 | -4 | 0 | 13 | 68 | -73 | 4 | -1 | 0 | 14 | 57 | 54 | 5 |
| 3 | 1 | 11 | 69 | 68 | 4 | 0 | -5 | 12 | 98 | -95 | 3 | 0 | 2 | 12 | 56 | 49 | 5 | -3 | 0 | 13 | 47 | -40 | 6 | 0 | 0 | 14 | 31 | -28 | -8 |
| 4 | 1 | 11 | 111 | -110 | 3 | 1 | -5 | 12 | 101 | -101 | 3 | 1 | 2 | 12 | 43 | -47 | 6 | -2 | 0 | 13 | 57 | 57 | 5 | 1 | 0 | 14 | 48 | 43 | 6 |
| 5 | 1 | 11 | 40 | -41 | 7 | 2 | -5 | 12 | 33 | 33 | -7 | 2 | 2 | 12 | 89 | 84 | 4 | -1 | 0 | 13 | 10 | 11 | -10 | 2 | 0 | 14 | 101 | -90 | 3 |
| 6 | 1 | 11 | 44 | -46 | 7 | 3 | -5 | 12 | 71 | -69 | 4 | 3 | 2 | 12 | 45 | 36 | 6 | 0 | 0 | 13 | 95 | 92 | 3 | -2 | -2 | 15 | 11 | -5 | -11 |
| 2 | 2 | 11 | 84 | 83 | 4 | 4 | -5 | 12 | 80 | 80 | 4 | -3 | -7 | 13 | 11 | 1 | -11 | 1 | 0 | 13 | 58 | 58 | 5 | -1 | -2 | 15 | 17 | 1 | -17 |
| 3 | 2 | 11 | 20 | 19 | -20 | 5 | -5 | 12 | 103 | 90 | 3 | -2 | -7 | 13 | 50 | -44 | 5 | 2 | 0 | 13 | 30 | -22 | -9 | 0 | -2 | 15 | 51 | -47 | 5 |
| 4 | 2 | 11 | 77 | 82 | 4 | 6 | -5 | 12 | 20 | -4 | -20 | -1 | -7 | 13 | 77 | -70 | 4 | 3 | 0 | 13 | 10 | 3 | -10 | 0 | -2 | 15 | 40 | 28 | 6 |
| -2 | -8 | 12 | 44 | 37 | 5 | 6 | -4 | 12 | 74 | 72 | 5 | 0 | -7 | 13 | 49 | 48 | 5 | 4 | 0 | 13 | 79 | -73 | 4 | 0 | -1 | 15 | | | |

THE STRUCTURE TOPOLOGY OF SIDPIETERSITE, $\text{Pb}^{2+}_4(\text{S}^{6+}\text{O}_3\text{S}^{2-})\text{O}_2(\text{OH})_2$, A NOVEL THIOSULFATE STRUCTURE

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ABSTRACT

The crystal structure of sidpietersite, $\text{Pb}^{2+}_4(\text{S}^{6+}\text{O}_3\text{S}^{2-})\text{O}_2(\text{OH})_2$, triclinic, a 7.455(2), b 6.496(2), c 11.207(4) Å, α 114.33(2), β 89.65(2), γ 88.69(2)°, V 494.3(3) Å³, $Z = 2$, space group $P\bar{1}$, has been solved by direct methods and refined to an R index of 3.0% for 1292 observed ($|F_o| > 5\sigma |F_c|$) reflections measured with $\text{MoK}\alpha$ X-radiation. There are four symmetrically distinct Pb sites occupied by Pb^{2+} in very asymmetric coordinations typical of stereoactive lone-pair behavior. Sidpietersite contains a thiosulfate group, $(\text{S}^{6+}\text{O}_3\text{S}^{2-})$, and is the first thiosulfate mineral to be characterized structurally. The $\langle \text{S}^{6+}-\text{O} \rangle$ distance is 1.48 Å, the $\text{S}^{6+}-\text{S}^{2-}$ distance is 1.98 Å, and the four anions form a distorted tetrahedral arrangement about the central cation. A ladder of Pb^{2+} and O atoms (a motif from the structure of PbO) extends along the a axis; this ladder is decorated by peripheral Pb atoms, and the resultant ribbons are cross-linked by thiosulfate groups to form a thick slab orthogonal to [001]. These slabs are linked along the c axis by weak $\text{Pb}-\text{S}^{2-}$ bonds. The structure of sidpietersite is unrelated to any synthetic thiosulfate structures. The latter have cation:thiosulfate ratios between 1:1 and 2:1, and the structures consist of thiosulfate groups linked by weak bonds. In sidpietersite, the cation:thiosulfate ratio is 4:1, and the cations form extended polymerized arrays that are cross-linked by thiosulfate groups. There seems no intrinsic reason why more complex structures such as sidpietersite should not occur, at least as synthetic materials.

Keywords: sidpietersite, thiosulfate, crystal structure, Pb mineral, Tsumeb, Namibia.

SOMMAIRE

Nous avons résolu la structure cristalline de la sidpietersite, $\text{Pb}^{2+}_4(\text{S}^{6+}\text{O}_3\text{S}^{2-})\text{O}_2(\text{OH})_2$, triclinique, a 7.455(2), b 6.496(2), c 11.207(4) Å, α 114.33(2), β 89.65(2), γ 88.69(2)°, V 494.3(3) Å³, $Z = 2$, groupe spatial $P\bar{1}$, par méthodes directes et affinement jusqu'à un résidu R de 3.0% pour 1292 réflexions observées ($|F_o| > 5\sigma |F_c|$) et mesurées avec rayonnement $\text{MoK}\alpha$. La structure contient quatre sites Pb symétriquement distincts, où sont logés les atomes Pb^{2+} dans une coordination asymétrique typique d'un comportement impliquant une paire d'électrons isolés stéréoactifs. La sidpietersite contient un groupe thiosulfate, $(\text{S}^{6+}\text{O}_3\text{S}^{2-})$, et en serait le premier exemple dans le règne minéral à être structuralement décrit. La distance $\langle \text{S}^{6+}-\text{O} \rangle$ est 1.48 Å, la distance $\text{S}^{6+}-\text{S}^{2-}$ est 1.98 Å, et les quatre anions sont disposés dans un agencement tétraédrique difforme autour du cation central. Une échelle d'atomes Pb^{2+} et O (motif retrouvé dans la structure de PbO) longe l'axe a , et est décoré par des atomes périphériques de Pb, et les rubans qui en résultent sont interliés par des groupes thiosulfatés pour former une épaisse couche perpendiculaire à [001]. Ces couches sont liées le long de l'axe c par de faibles liaisons $\text{Pb}-\text{S}^{2-}$. Du point de vue structural, la sidpietersite ne ressemble à aucun composé thiosulfaté synthétique. Ce groupe de composés possède un rapport cation:thiosulfate entre 1:1 et 2:1, et leurs structures comportent des agencements de groupes thiosulfate liés par de faibles liaisons. Dans la sidpietersite, le rapport cation:thiosulfate est 4:1, et les cations forment des agencements allongés polymérisés, interliés par des groupes thiosulfatés. Il ne semble pas y avoir une raison intrinsèque pour empêcher la formation de structures plus complexes, comme celle de la sidpietersite, au moins parmi les matériaux synthétiques.

(Traduit par la Rédaction)

Mots-clés: sidpietersite, thiosulfate, structure cristalline, minéral de plomb, Tsumeb, Namibie.

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