# inorganic compounds

# Langbeinite-type $Rb_2Ca_2(SO_4)_3$

## Mohamed Boujelben,* Mohamed Toumi and Tahar Mhiri

Laboratoire de l'Etat Solide, Faculté des Sciences de Sfax, 3018 Sfax, Tunisia

Correspondence e-mail: m_boujelbene2010@yahoo.fr

Single crystals of dirubidium dicalcium tris[sulfate(VI)], $Rb_2Ca_2(SO_4)_3$, were obtained from solid-state reactions of $Rb_2SO_4$ and $CaSO_4$. The title compound crystallizes in the cubic langbeinite-type structure. It features two crystallographically independent $CaO_6$ octahedra (each with site symmetry 3), which are linked by sharing corners with $SO_4$ tetrahedra to establish a framework with composition $[Ca_2(SO_4)_3]^{2-}$, where the two independent $Rb^+$ cations (site symmetry 3) are located in the voids.

## Related literature

For studies of phase transitions of langbeinites, see: Ukeda *et al.* (1995); Dilanian *et al.* (1999). Double sulfates of the langbeinite-type were summarized by Gattow & Zemann (1957). For single-crystal structure analyses of selected langbeinites, see: Zemann & Zemann (1957); Guelylah *et al.* (1996); Guelylah & Madariaga (2003). Differences between the langbeinite and the Nasicon structure are discussed by Sizova *et al.* (1981) and Droß & Glaum (2004). Parameters for the bond valence sum (BVS) analysis were taken from Brown & Altermatt (1985).

## Experimental

### Crystal data

| | |
|---|---|
| $Rb_2Ca_2(SO_4)_3$ | $Z$ = 4 |
| $M_r$ = 539.28 | Mo $K\alpha$ radiation |
| Cubic, $P2_13$ | $\mu$ = 9.79 mm$^{-1}$ |
| $a$ = 10.553 (3) Å | $T$ = 293 K |
| $V$ = 1175.2 (6) Å$^3$ | $0.22 \times 0.13 \times 0.05$ mm |

### Data collection

| | |
|---|---|
| Stoe–Siemens AED2 four-circle diffractometer | Spek, 2003) |
| | $T_{min}$ = 0.231, $T_{max}$ = 0.644 |
| Absorption correction: multi-scan (*MULABS* in *PLATON*; | 1236 measured reflections |
| | 1080 independent reflections |

| | |
|---|---|
| 658 reflections with $I > 3\sigma(I)$ | 2 standard reflections |
| $R_{int}$ = 0.08 | frequency: 30 min |
| | intensity decay: 0.7% |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.065 | $\Delta\rho_{max}$ = 0.93 e Å$^{-3}$ |
| $wR(F^2)$ = 0.128 | $\Delta\rho_{min}$ = −1.00 e Å$^{-3}$ |
| $S$ = 1.12 | Absolute structure: Flack (1983), |
| 1080 reflections | 558 Friedel pairs |
| 59 parameters | Flack parameter: 0.00 (4) |

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Ca1—O4 | 2.284 (10) | Rb2—O2 | 3.018 (10) |
| Ca1—O3$^i$ | 2.299 (10) | Rb2—O1$^{vii}$ | 3.118 (10) |
| Ca2—O1$^{ii}$ | 2.304 (9) | Rb2—O3$^{vii}$ | 3.338 (11) |
| Ca2—O2$^{iii}$ | 2.338 (9) | S—O1$^{viii}$ | 1.449 (9) |
| Rb1—O4$^{iv}$ | 3.028 (11) | S—O2 | 1.447 (9) |
| Rb1—O1$^v$ | 3.224 (9) | S—O3$^{viii}$ | 1.456 (9) |
| Rb1—O3$^v$ | 3.239 (12) | S—O4 | 1.466 (10) |
| Rb1—O3$^{vi}$ | 3.464 (13) | | |

Symmetry codes: (i) $z - \frac{1}{2}, -x + \frac{1}{2}, -y + 1$; (ii) $-z + \frac{3}{2}, -x + 1, y + \frac{1}{2}$; (iii) $-y + 1, z + \frac{1}{2}, -x + \frac{1}{2}$; (iv) $-z + 1, x + \frac{1}{2}, -y + \frac{3}{2}$; (v) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (vi) $-z + 2, x + \frac{1}{2}, -y + \frac{3}{2}$; (vii) $-z + 1, x - \frac{1}{2}, -y + \frac{1}{2}$; (viii) $x, y, z - 1$.

Data collection: *STADI4* (Stoe & Cie, 2000); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *CRYSTALS*.

## References

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Brandenburg, K. & Berndt, M. (1999). *DIAMOND*. Version 2.1.b. Crystal Impact GbR, Bonn, Germany.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Dilanian, R. A., Izumi, F., Kamiyama, T. & Itoh, K. (1999). *J. Phys. Chem. Solids*, **60**, 1423–1426.

Droß, T. & Glaum, R. (2004). *Acta Cryst.* E**60**, i58–i60.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Gattow, V. G. & Zemann, J. (1957). *Z. Anorg. Allg. Chem.* **293**, 233–240.

Guelylah, A. & Madariaga, G. (2003). *Acta Cryst.* C**59**, i32–i34.

Guelylah, A., Madariaga, G. & Breczewski, T. (1996). *Acta Cryst.* C**52**, 2954–2956.

Sheldrick, G. M. (1997). *SHELXS97*. University of Göttingen, Germany.

Sizova, R. G., Blinov, V. A., Voronkov, A. A., Ilyukhin, V. V. & Belov, N. V. (1981). *Kristallografiya*, **26**, 293–300. (In Russian.)

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Stoe & Cie (1996). *X-RED*. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (2000). *STADI4*. Stoe & Cie, Darmstadt, Germany.

Ukeda, T., Itoh, K. & Moriyoshi, C. (1995). *J. Phys. Soc. Jpn*, **64**, 504–512.

Zemann, A. & Zemann, J. (1957). *Acta Cryst.* **10**, 409–413.

**supplementary materials**

# Langbeinite-type Rb$_2$Ca$_2$(SO$_4$)$_3$

## M. Boujelben, M. Toumi and T. Mhiri

## Comment

The double sulfate salts with formula A$_2$B$_2$(SO$_4$)$_3$ adopting the langbeinite-type structure have attracted great interest due to their ferroelastic or ferroelectric properties and first-order phase transitions (Ukeda *et al.*, 1995; Dilanian *et al.*, 1999 and references therein). Numerous compounds with A = NH$_4$, K, Rb, Tl, Cs and B = Mn, Ca, Mg, Fe, Co, Ni, Zn, Cd (*e.g.* Zemann & Zemann, 1957; Guelylah *et al.*, 1996; Guelylah & Madariaga, 2003) have been characterized up to now. Gattow and Zemann (1957) mentioned the possible synthesis of 26 double sulfates, including large monovalent cations. Notable differences exist between langbeinite-type and Nasicon-type structures (Sizova *et al.*, 1981; Droß & Glaum, 2004). In the Nasicon-type structures, four interstitial vacant sites are present, while langbeinite-type structures have only two.

A projection of the crystal structure of langbeinite-type Rb$_2$Ca$_2$(SO$_4$)$_3$ is given in Fig. 1. It is characterized by the presence of alternating SO$_4$ tetrahedra and CaO$_6$ octahedra, linked by sharing corners, to establish a [Ca$_2$(SO$_4$)$_3$]$^{2-}$ framework. The two independent Rb$^+$ ions are located in the voids of this arrangement.

The SO$_4$ tetrahedra are quite regular, with an average S—O distance of 1.455 Å, which is virtually the same as that observed in the isotypic Rb$_2$Cd$_2$(SO$_4$)$_2$ (1.455 Å; Guelylah & Madariaga, 2003). In the title compound sulfur has a bond valence sum (BVS) of 6.69 valence units (expected 6) as calculated with the values given by Brown & Altermatt (1985). The [Ca1O$_6$] octahedron is quite regular, with d$_{av}$(Ca1—O) = 2.292 Å, whereas the [Ca2O$_6$] octahedron is considerably distorted, with d$_{av}$(Ca2—O) = 2.321 Å. Rb$_1$ has twelve oxygen neighbours with d$_{av}$(Rb1—O) = 3.239 Å and a BVS of 1.03 (expected 1). Rb$_2$ is ninefold coordinated with d$_{av}$(Rb2—O) = 3.158 Å and a BVS of 0.852 (expected 1).

## Experimental

Single crystals of Rb$_2$Ca$_2$(SO$_4$)$_3$ were obtained by solid-state reaction of Rb$_2$SO$_4$ (Aldrich 99.999%) and CaSO$_4$.H$_2$O (Aldrich 99.9%). Stoichiometric amounts of the starting materials were mixed thoroughly in an agate mortar. After grinding, the mixture was heated at 673 K for 4 h, then at 1173 K for 66 h and was finally allowed to cool to room temperature at a rate of 5 K/h. Transparent polycrystalline chunks were obtained from which single crystals were separated manually.
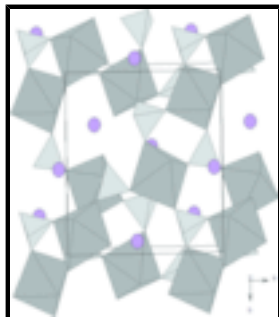
# supplementary materials

**Figures**



Fig. 1. Projection of the crystal structure of langbeinite-type $Rb_2Ca_2(SO_4)_3$ approximately along [001]. The voids are visible, where the $Rb^+$ cations (lavender spheres) are located. $CaO_6$ octahedra are dark-grey and $SO_4$ tetrahedra are light-grey.

**dirubidium dicalcium tris[sulfate(VI)]**

*Crystal data*

| | |
|---|---|
| $Rb_2Ca_2(SO_4)_3$ | $Z = 4$ |
| $M_r = 539.28$ | $F_{000} = 1032$ |
| Cubic, $P2_13$ | $D_x = 3.048$ Mg m$^{-3}$ |
| Hall symbol: P 2ac 2ab 3 | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| $a = 10.553$ (3) Å | Cell parameters from 23 reflections |
| $b = 10.553$ (3) Å | $\theta = 2.7–30.1°$ |
| $c = 10.553$ (3) Å | $\mu = 9.79$ mm$^{-1}$ |
| $\alpha = 90°$ | $T = 293$ K |
| $\beta = 90°$ | Fragment, colourless |
| $\gamma = 90°$ | $0.22 \times 0.13 \times 0.05$ mm |
| $V = 1175.2$ (6) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Stoe–Siemens AED2 four-circle diffractometer | $R_{int} = 0.08$ |
| Monochromator: graphite | $\theta_{max} = 29.9°$ |
| $T = 298$ K | $\theta_{min} = 2.7°$ |
| $\omega/2\theta$ scans | $h = -8 \rightarrow 9$ |
| Absorption correction: multi-scan (MULABS in PLATON; Spek, 2003) | $k = -10 \rightarrow 10$ |
| $T_{min} = 0.231$, $T_{max} = 0.644$ | $l = -14 \rightarrow 14$ |
| 1236 measured reflections | 2 standard reflections |
| 1080 independent reflections | every 30 min |
| 658 reflections with $I > 3\sigma(I)$ | intensity decay: 0.7% |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o{}^2) + (0.021P)^2 + 6.5703P]$ |

where $P = (F_o{}^2 + 2F_c{}^2)/3$ Method, part 1, Chebychev polynomial, (Watkin (1994). Acta Cryst. A50, 411–437. *P*rince (1982) Mathematical Techniques in Crystallography and Materials Science. Ne*w* York: Springer-Verlag.] [*w*eight] = $1.0/[A_0*T_0(x) + A_1*T_1(x) \cdots + A_{n-1}]*T_{n-1}(x)]$

where $A_i$ are the Chebychev coefficients listed be-lo*w* and x = $F$ /$F$max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * $[1-(deltaF/6*sigmaF)^2]^2$ $A_i$ are: 2.38 -2.95 2.50 -1.02 0.340

| | |
|---|---|
| Least-squares matrix: full | $(\Delta/\sigma)_{max} = 0.001$ |
| $R[F^2 > 2\sigma(F^2)] = 0.065$ | $\Delta\rho_{max} = 0.93$ e Å$^{-3}$ |
| $wR(F^2) = 0.128$ | $\Delta\rho_{min} = -1.00$ e Å$^{-3}$ |
| $S = 1.12$ | Extinction correction: SHELXL |
| 1080 reflections | Extinction coefficient: 0.0008 (5) |
| 59 parameters | Absolute structure: Flack (1983), 558 Friedel pairs |
| Primary atom site location: structure-invariant direct methods | Flack parameter: 0.00 (4) |

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| Ca1 | 0.3314 (2) | 0.3314 (2) | 0.3314 (2) | 0.0170 (9) |
| Ca2 | 0.5920 (2) | 0.5920 (2) | 0.5920 (2) | 0.0170 (9) |
| Rb1 | 0.81628 (13) | 0.81628 (13) | 0.81628 (13) | 0.0270 (5) |
| Rb2 | 0.04991 (13) | 0.04991 (13) | 0.04991 (13) | 0.0291 (6) |
| S | 0.2243 (3) | 0.3749 (3) | 0.0108 (3) | 0.0136 (6) |
| O1 | 0.3089 (9) | 0.2795 (8) | 0.9600 (9) | 0.032 (2) |
| O2 | 0.0954 (8) | 0.3285 (10) | 0.0046 (10) | 0.039 (3) |
| O3 | 0.2364 (10) | 0.4880 (10) | 0.9326 (11) | 0.043 (3) |
| O4 | 0.2580 (10) | 0.4059 (11) | 0.1420 (9) | 0.044 (3) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ca1 | 0.0170 (9) | 0.0170 (9) | 0.0170 (9) | −0.0002 (10) | −0.0002 (10) | −0.0002 (10) |
| Ca2 | 0.0170 (9) | 0.0170 (9) | 0.0170 (9) | −0.0004 (10) | −0.0004 (10) | −0.0004 (10) |
| Rb1 | 0.0270 (5) | 0.0270 (5) | 0.0270 (5) | −0.0023 (6) | −0.0023 (6) | −0.0023 (6) |
| Rb2 | 0.0291 (6) | 0.0291 (6) | 0.0291 (6) | 0.0012 (6) | 0.0012 (6) | 0.0012 (6) |
| S | 0.0156 (15) | 0.0120 (13) | 0.0131 (15) | 0.0031 (11) | 0.0003 (11) | 0.0015 (10) |
| O1 | 0.034 (5) | 0.023 (5) | 0.039 (6) | 0.011 (4) | 0.012 (5) | −0.006 (4) |
| O2 | 0.015 (5) | 0.037 (6) | 0.064 (7) | −0.007 (4) | 0.011 (5) | −0.016 (6) |
| O3 | 0.059 (7) | 0.030 (6) | 0.041 (6) | 0.015 (5) | 0.008 (5) | 0.023 (5) |
| O4 | 0.060 (8) | 0.047 (7) | 0.026 (6) | −0.003 (6) | −0.009 (5) | −0.011 (5) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Ca1—O4[i] | 2.284 (10) | Rb1—O3[xxiii] | 3.464 (13) |
| Ca1—O4[ii] | 2.284 (10) | Rb1—O3[xxiv] | 3.464 (13) |

| | | | |
|---|---|---|---|
| Ca1—O4 | 2.284 (10) | Rb2—O2$^{i}$ | 3.018 (10) |
| Ca1—O3$^{iii}$ | 2.299 (10) | Rb2—O2 | 3.018 (10) |
| Ca1—O3$^{iv}$ | 2.299 (10) | Rb2—O2$^{ii}$ | 3.018 (10) |
| Ca1—O3$^{v}$ | 2.299 (10) | Rb2—O1$^{xxv}$ | 3.118 (10) |
| Ca1—Rb1$^{vi}$ | 4.0344 (18) | Rb2—O1$^{xxvi}$ | 3.118 (10) |
| Ca1—Rb1$^{vii}$ | 4.0344 (18) | Rb2—O1$^{xxvii}$ | 3.118 (10) |
| Ca1—Rb1$^{viii}$ | 4.0344 (18) | Rb2—O3$^{xxvi}$ | 3.338 (11) |
| Ca1—Rb2$^{ix}$ | 4.804 (2) | Rb2—O3$^{xxvii}$ | 3.338 (11) |
| Ca1—Rb2$^{x}$ | 4.804 (2) | Rb2—O3$^{xxv}$ | 3.338 (11) |
| Ca1—Rb2$^{xi}$ | 4.804 (2) | Rb2—S$^{xxviii}$ | 3.584 (3) |
| Ca2—O1$^{xii}$ | 2.304 (9) | Rb2—S$^{xxix}$ | 3.584 (3) |
| Ca2—O1$^{xiii}$ | 2.304 (9) | Rb2—S$^{xxx}$ | 3.584 (3) |
| Ca2—O1$^{xiv}$ | 2.304 (9) | S—O1$^{xxxi}$ | 1.449 (9) |
| Ca2—O2$^{xv}$ | 2.338 (9) | S—O2 | 1.447 (9) |
| Ca2—O2$^{xvi}$ | 2.338 (9) | S—O3$^{xxxi}$ | 1.456 (10) |
| Ca2—O2$^{xvii}$ | 2.338 (9) | S—O4 | 1.466 (10) |
| Ca2—S$^{xv}$ | 3.464 (4) | S—Ca2$^{xxvii}$ | 3.464 (4) |
| Ca2—S$^{xvi}$ | 3.464 (4) | S—Rb1$^{v}$ | 3.533 (3) |
| Ca2—S$^{xvii}$ | 3.464 (4) | S—Rb2$^{xi}$ | 3.584 (3) |
| Ca2—Rb2$^{xv}$ | 4.0891 (19) | S—Rb1$^{viii}$ | 3.859 (3) |
| Ca2—Rb2$^{xviii}$ | 4.0891 (19) | O1—S$^{xxxii}$ | 1.449 (9) |
| Ca2—Rb2$^{xvii}$ | 4.0891 (19) | O1—Ca2$^{vii}$ | 2.304 (9) |
| Rb1—O4$^{xix}$ | 3.028 (11) | O1—Rb2$^{xv}$ | 3.118 (10) |
| Rb1—O4$^{xx}$ | 3.028 (11) | O1—Rb1$^{vii}$ | 3.224 (9) |
| Rb1—O4$^{xxi}$ | 3.028 (11) | O2—Ca2$^{xxvii}$ | 2.338 (9) |
| Rb1—O1$^{xii}$ | 3.224 (9) | O2—Rb1$^{v}$ | 3.515 (10) |
| Rb1—O1$^{xiii}$ | 3.224 (9) | O3—S$^{xxxii}$ | 1.456 (10) |
| Rb1—O1$^{xiv}$ | 3.224 (10) | O3—Ca1$^{xviii}$ | 2.299 (10) |
| Rb1—O3$^{xiv}$ | 3.239 (12) | O3—Rb1$^{vii}$ | 3.239 (12) |
| Rb1—O3$^{xii}$ | 3.239 (12) | O3—Rb2$^{xv}$ | 3.338 (11) |
| Rb1—O3$^{xiii}$ | 3.239 (12) | O3—Rb1$^{xxxiii}$ | 3.464 (13) |
| Rb1—O3$^{xxii}$ | 3.464 (13) | O4—Rb1$^{viii}$ | 3.028 (11) |
| O4$^{i}$—Ca1—O4$^{ii}$ | 96.9 (4) | O3$^{xii}$—Rb1—O3$^{xxiii}$ | 138.68 (19) |
| O4$^{i}$—Ca1—O4 | 96.9 (4) | O3$^{xiii}$—Rb1—O3$^{xxiii}$ | 58.5 (4) |
| O4$^{ii}$—Ca1—O4 | 96.9 (4) | O3$^{xxii}$—Rb1—O3$^{xxiii}$ | 82.8 (3) |
| O4$^{i}$—Ca1—O3$^{iii}$ | 90.9 (4) | O4$^{xix}$—Rb1—O3$^{xxiv}$ | 107.7 (3) |
| O4$^{ii}$—Ca1—O3$^{iii}$ | 81.3 (4) | O4$^{xx}$—Rb1—O3$^{xxiv}$ | 54.3 (3) |
| O4—Ca1—O3$^{iii}$ | 172.1 (4) | O4$^{xxi}$—Rb1—O3$^{xxiv}$ | 42.4 (2) |
| O4$^{i}$—Ca1—O3$^{iv}$ | 81.3 (4) | O1$^{xii}$—Rb1—O3$^{xxiv}$ | 96.7 (2) |
| O4$^{ii}$—Ca1—O3$^{iv}$ | 172.1 (4) | O1$^{xiii}$—Rb1—O3$^{xxiv}$ | 131.6 (2) |

| | | | |
|---|---|---|---|
| O4—Ca1—O3$^{iv}$ | 90.9 (4) | O1$^{xiv}$—Rb1—O3$^{xxiv}$ | 145.4 (2) |
| O3$^{iii}$—Ca1—O3$^{iv}$ | 91.0 (4) | O3$^{xiv}$—Rb1—O3$^{xxiv}$ | 138.68 (19) |
| O4$^{i}$—Ca1—O3$^{v}$ | 172.1 (4) | O3$^{xii}$—Rb1—O3$^{xxiv}$ | 58.5 (4) |
| O4$^{ii}$—Ca1—O3$^{v}$ | 90.9 (4) | O3$^{xiii}$—Rb1—O3$^{xxiv}$ | 104.18 (3) |
| O4—Ca1—O3$^{v}$ | 81.3 (4) | O3$^{xxii}$—Rb1—O3$^{xxiv}$ | 82.8 (3) |
| O3$^{iii}$—Ca1—O3$^{v}$ | 91.0 (4) | O3$^{xxiii}$—Rb1—O3$^{xxiv}$ | 82.8 (3) |
| O3$^{iv}$—Ca1—O3$^{v}$ | 91.0 (4) | O2$^{i}$—Rb2—O2 | 91.4 (3) |
| O1$^{xii}$—Ca2—O1$^{xiii}$ | 85.6 (4) | O2$^{i}$—Rb2—O2$^{ii}$ | 91.4 (3) |
| O1$^{xii}$—Ca2—O1$^{xiv}$ | 85.6 (4) | O2—Rb2—O2$^{ii}$ | 91.4 (3) |
| O1$^{xiii}$—Ca2—O1$^{xiv}$ | 85.6 (4) | O2$^{i}$—Rb2—O1$^{xxv}$ | 64.0 (2) |
| O1$^{xii}$—Ca2—O2$^{xv}$ | 172.2 (4) | O2—Rb2—O1$^{xxv}$ | 153.1 (3) |
| O1$^{xiii}$—Ca2—O2$^{xv}$ | 88.5 (3) | O2$^{ii}$—Rb2—O1$^{xxv}$ | 79.1 (2) |
| O1$^{xiv}$—Ca2—O2$^{xv}$ | 89.0 (3) | O2$^{i}$—Rb2—O1$^{xxvi}$ | 79.1 (2) |
| O1$^{xii}$—Ca2—O2$^{xvi}$ | 89.0 (3) | O2—Rb2—O1$^{xxvi}$ | 64.0 (2) |
| O1$^{xiii}$—Ca2—O2$^{xvi}$ | 172.2 (4) | O2$^{ii}$—Rb2—O1$^{xxvi}$ | 153.1 (3) |
| O1$^{xiv}$—Ca2—O2$^{xvi}$ | 88.5 (3) | O1$^{xxv}$—Rb2—O1$^{xxvi}$ | 117.59 (9) |
| O2$^{xv}$—Ca2—O2$^{xvi}$ | 96.4 (3) | O2$^{i}$—Rb2—O1$^{xxvii}$ | 153.1 (3) |
| O1$^{xii}$—Ca2—O2$^{xvii}$ | 88.5 (3) | O2—Rb2—O1$^{xxvii}$ | 79.1 (2) |
| O1$^{xiii}$—Ca2—O2$^{xvii}$ | 89.0 (3) | O2$^{ii}$—Rb2—O1$^{xxvii}$ | 64.0 (2) |
| O1$^{xiv}$—Ca2—O2$^{xvii}$ | 172.2 (4) | O1$^{xxv}$—Rb2—O1$^{xxvii}$ | 117.59 (9) |
| O2$^{xv}$—Ca2—O2$^{xvii}$ | 96.4 (3) | O1$^{xxvi}$—Rb2—O1$^{xxvii}$ | 117.59 (9) |
| O2$^{xvi}$—Ca2—O2$^{xvii}$ | 96.4 (3) | O2$^{i}$—Rb2—O3$^{xxvi}$ | 78.9 (3) |
| O4$^{xix}$—Rb1—O4$^{xx}$ | 94.9 (3) | O2—Rb2—O3$^{xxvi}$ | 106.5 (2) |
| O4$^{xix}$—Rb1—O4$^{xxi}$ | 94.9 (3) | O2$^{ii}$—Rb2—O3$^{xxvi}$ | 159.8 (2) |
| O4$^{xx}$—Rb1—O4$^{xxi}$ | 94.9 (3) | O1$^{xxv}$—Rb2—O3$^{xxvi}$ | 80.6 (2) |
| O4$^{xix}$—Rb1—O1$^{xii}$ | 155.6 (3) | O1$^{xxvi}$—Rb2—O3$^{xxvi}$ | 42.5 (2) |
| O4$^{xx}$—Rb1—O1$^{xii}$ | 99.5 (2) | O1$^{xxvii}$—Rb2—O3$^{xxvi}$ | 127.9 (3) |
| O4$^{xxi}$—Rb1—O1$^{xii}$ | 103.3 (3) | O2$^{i}$—Rb2—O3$^{xxvii}$ | 159.8 (2) |
| O4$^{xix}$—Rb1—O1$^{xiii}$ | 103.3 (3) | O2—Rb2—O3$^{xxvii}$ | 78.9 (3) |
| O4$^{xx}$—Rb1—O1$^{xiii}$ | 155.6 (3) | O2$^{ii}$—Rb2—O3$^{xxvii}$ | 106.5 (2) |
| O4$^{xxi}$—Rb1—O1$^{xiii}$ | 99.5 (2) | O1$^{xxv}$—Rb2—O3$^{xxvii}$ | 127.9 (3) |
| O1$^{xii}$—Rb1—O1$^{xiii}$ | 58.1 (3) | O1$^{xxvi}$—Rb2—O3$^{xxvii}$ | 80.6 (2) |
| O4$^{xix}$—Rb1—O1$^{xiv}$ | 99.5 (2) | O1$^{xxvii}$—Rb2—O3$^{xxvii}$ | 42.5 (2) |
| O4$^{xx}$—Rb1—O1$^{xiv}$ | 103.3 (3) | O3$^{xxvi}$—Rb2—O3$^{xxvii}$ | 86.7 (3) |
| O4$^{xxi}$—Rb1—O1$^{xiv}$ | 155.6 (3) | O2$^{i}$—Rb2—O3$^{xxv}$ | 106.5 (2) |
| O1$^{xii}$—Rb1—O1$^{xiv}$ | 58.1 (3) | O2—Rb2—O3$^{xxv}$ | 159.8 (2) |
| O1$^{xiii}$—Rb1—O1$^{xiv}$ | 58.1 (3) | O2$^{ii}$—Rb2—O3$^{xxv}$ | 78.9 (3) |
| O4$^{xix}$—Rb1—O3$^{xiv}$ | 62.7 (3) | O1$^{xxv}$—Rb2—O3$^{xxv}$ | 42.5 (2) |
| O4$^{xx}$—Rb1—O3$^{xiv}$ | 85.4 (3) | O1$^{xxvi}$—Rb2—O3$^{xxv}$ | 127.9 (3) |
| O4$^{xxi}$—Rb1—O3$^{xiv}$ | 157.5 (3) | O1$^{xxvii}$—Rb2—O3$^{xxv}$ | 80.6 (2) |
| O1$^{xii}$—Rb1—O3$^{xiv}$ | 98.8 (3) | O3$^{xxvi}$—Rb2—O3$^{xxv}$ | 86.7 (3) |

| | | | |
|---|---|---|---|
| O1$^{xiii}$—Rb1—O3$^{xiv}$ | 88.6 (2) | O3$^{xxvii}$—Rb2—O3$^{xxv}$ | 86.7 (3) |
| O1$^{xiv}$—Rb1—O3$^{xiv}$ | 42.6 (2) | O1$^{xxxi}$—S—O2 | 109.1 (6) |
| O4$^{xix}$—Rb1—O3$^{xii}$ | 157.5 (3) | O1$^{xxxi}$—S—O3$^{xxxi}$ | 107.8 (6) |
| O4$^{xx}$—Rb1—O3$^{xii}$ | 62.7 (3) | O2—S—O3$^{xxxi}$ | 109.5 (7) |
| O4$^{xxi}$—Rb1—O3$^{xii}$ | 85.4 (3) | O1$^{xxxi}$—S—O4 | 110.8 (6) |
| O1$^{xii}$—Rb1—O3$^{xii}$ | 42.6 (2) | O2—S—O4 | 110.2 (6) |
| O1$^{xiii}$—Rb1—O3$^{xii}$ | 98.8 (2) | O3$^{xxxi}$—S—O4 | 109.3 (7) |
| O1$^{xiv}$—Rb1—O3$^{xii}$ | 88.6 (2) | S$^{xxxii}$—O1—Ca2$^{vii}$ | 164.7 (6) |
| O3$^{xiv}$—Rb1—O3$^{xii}$ | 114.23 (15) | S$^{xxxii}$—O1—Rb2$^{xv}$ | 96.5 (4) |
| O4$^{xix}$—Rb1—O3$^{xiii}$ | 85.4 (3) | Ca2$^{vii}$—O1—Rb2$^{xv}$ | 96.8 (3) |
| O4$^{xx}$—Rb1—O3$^{xiii}$ | 157.5 (3) | S$^{xxxii}$—O1—Rb1$^{vii}$ | 89.9 (4) |
| O4$^{xxi}$—Rb1—O3$^{xiii}$ | 62.7 (3) | Ca2$^{vii}$—O1—Rb1$^{vii}$ | 94.3 (3) |
| O1$^{xii}$—Rb1—O3$^{xiii}$ | 88.6 (2) | Rb2$^{xv}$—O1—Rb1$^{vii}$ | 103.6 (3) |
| O1$^{xiii}$—Rb1—O3$^{xiii}$ | 42.6 (2) | S—O2—Ca2$^{xxvii}$ | 131.0 (6) |
| O1$^{xiv}$—Rb1—O3$^{xiii}$ | 98.8 (3) | S—O2—Rb2 | 118.2 (5) |
| O3$^{xiv}$—Rb1—O3$^{xiii}$ | 114.23 (15) | Ca2$^{xxvii}$—O2—Rb2 | 98.8 (3) |
| O3$^{xii}$—Rb1—O3$^{xiii}$ | 114.23 (14) | S—O2—Rb1$^{v}$ | 78.8 (4) |
| O4$^{xix}$—Rb1—O3$^{xxii}$ | 54.3 (3) | Ca2$^{xxvii}$—O2—Rb1$^{v}$ | 128.1 (4) |
| O4$^{xx}$—Rb1—O3$^{xxii}$ | 42.4 (2) | Rb2—O2—Rb1$^{v}$ | 99.1 (3) |
| O4$^{xxi}$—Rb1—O3$^{xxii}$ | 107.7 (3) | S$^{xxxii}$—O3—Ca1$^{xviii}$ | 156.2 (7) |
| O1$^{xii}$—Rb1—O3$^{xxii}$ | 131.6 (2) | S$^{xxxii}$—O3—Rb1$^{vii}$ | 89.2 (5) |
| O1$^{xiii}$—Rb1—O3$^{xxii}$ | 145.4 (2) | Ca1$^{xviii}$—O3—Rb1$^{vii}$ | 91.9 (4) |
| O1$^{xiv}$—Rb1—O3$^{xxii}$ | 96.7 (2) | S$^{xxxii}$—O3—Rb2$^{xv}$ | 87.6 (5) |
| O3$^{xiv}$—Rb1—O3$^{xxii}$ | 58.5 (4) | Ca1$^{xviii}$—O3—Rb2$^{xv}$ | 115.7 (4) |
| O3$^{xii}$—Rb1—O3$^{xxii}$ | 104.18 (3) | Rb1$^{vii}$—O3—Rb2$^{xv}$ | 98.5 (3) |
| O3$^{xiii}$—Rb1—O3$^{xxii}$ | 138.68 (19) | S$^{xxxii}$—O3—Rb1$^{xxxiii}$ | 94.4 (5) |
| O4$^{xix}$—Rb1—O3$^{xxiii}$ | 42.4 (2) | Ca1$^{xviii}$—O3—Rb1$^{xxxiii}$ | 86.4 (3) |
| O4$^{xx}$—Rb1—O3$^{xxiii}$ | 107.7 (3) | Rb1$^{vii}$—O3—Rb1$^{xxxiii}$ | 174.7 (3) |
| O4$^{xxi}$—Rb1—O3$^{xxiii}$ | 54.3 (3) | Rb2$^{xv}$—O3—Rb1$^{xxxiii}$ | 77.7 (3) |
| O1$^{xii}$—Rb1—O3$^{xxiii}$ | 145.4 (2) | S—O4—Ca1 | 146.3 (7) |
| O1$^{xiii}$—Rb1—O3$^{xxiii}$ | 96.7 (2) | S—O4—Rb1$^{viii}$ | 113.7 (6) |
| O1$^{xiv}$—Rb1—O3$^{xxiii}$ | 131.6 (2) | Ca1—O4—Rb1$^{viii}$ | 97.9 (3) |
| O3$^{xiv}$—Rb1—O3$^{xxiii}$ | 104.18 (3) | | |

Symmetry codes: (i) $z, x, y$; (ii) $y, z, x$; (iii) $z−1/2, −x+1/2, −y+1$; (iv) $−x+1/2, −y+1, z−1/2$; (v) $−y+1, z−1/2, −x+1/2$; (vi) $−y+3/2, −z+1, x−1/2$; (vii) $−y+1, z−1/2, −x+3/2$; (viii) $z−1/2, −x+3/2, −y+1$; (ix) $−y, z+1/2, −x+1/2$; (x) $−y+1/2, −z, x+1/2$; (xi) $z+1/2, −x+1/2, −y$; (xii) $−x+1, y+1/2, −z+3/2$; (xiii) $y+1/2, −z+3/2, −x+1$; (xiv) $−z+3/2, −x+1, y+1/2$; (xv) $z+1/2, −x+1/2, −y+1$; (xvi) $−x+1/2, −y+1, z+1/2$; (xvii) $−y+1, z+1/2, −x+1/2$; (xviii) $−y+1/2, −z+1, x+1/2$; (xix) $−z+1, x+1/2, −y+3/2$; (xx) $x+1/2, −y+3/2, −z+1$; (xxi) $−y+3/2, −z+1, x+1/2$; (xxii) $x+1/2, −y+3/2, −z+2$; (xxiii) $−z+2, x+1/2, −y+3/2$; (xxiv) $−y+3/2, −z+2, x+1/2$; (xxv) $−z+1, x−1/2, −y+1/2$; (xxvi) $x−1/2, −y+1/2, −z+1$; (xxvii) $−y+1/2, −z+1, x−1/2$; (xxviii) $−z, x−1/2, −y+1/2$; (xxix) $x−1/2, −y+1/2, −z$; (xxx) $−y+1/2, −z, x−1/2$; (xxxi) $x, y, z−1$; (xxxii) $x, y, z+1$; (xxxiii) $z−1/2, −x+3/2, −y+2$.

**Fig. 1**