

elongated octahedron with the four nearest-neighbouring La atoms. The accommodation of Cl atoms in tunnels running in the  $z$  direction explains the high value of the  $U_{33}$  anisotropic thermal parameter.

The close similarity of the powder patterns of the  $\text{Ln}_3(\text{SiO}_4)_2\text{Cl}$  ( $\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}$ ) and  $\text{Ln}_3(\text{SiO}_4)_2\text{Br}$  ( $\text{Ln} = \text{La}, \text{Ce}$ ) phases shows that these halosilicates are isostructural with  $\text{La}_3(\text{SiO}_4)_2\text{Cl}$ . Their lattice constants will be published elsewhere, with those of other phases in the  $\text{Ln}_2\text{O}_3\text{-SiO}_2\text{-LnCl}_3$  systems. From samarium in the lanthanide series the chlorosilicates belong to the  $\text{Yb}_3(\text{SiO}_4)_2\text{Cl}$  type.

The two structures have common features: (1) the existence of double layers  $[\text{Ln}(\text{SiO}_4)]_n$  alternating with  $(\text{LnCl})_n$  layers; (2) the presence of tunnels accommodating the Cl atoms; (3) the square coordination of Cl.

However, the arrangement of ions in the  $[\text{Ln}(\text{SiO}_4)]_n$  and  $(\text{LnCl})_n$  planes differs. A higher coordination for  $\text{La}^{3+}$  is obtained by the increasing number of  $\text{SiO}_4$  groups connected by edge sharing to the rare-earth coordination polyhedra: three for La(1) and four for La(2) compared with two for Yb(1) and Yb(2).

The  $\text{SiO}_4$  tetrahedra are more regular for the La chlorosilicate than for the Yb phase. The Si—O bonds range from 1.61 to 1.64 Å ( $\langle\text{Si—O}\rangle$ : 1.626 Å) in the La phase and from 1.56 to 1.64 Å ( $\langle\text{Si—O}\rangle$ : 1.605 Å) in the Yb phase, and the O—Si—O angles from 106.6 to 117.7° ( $\langle\text{O—Si—O}\rangle$ : 109.4°) and from 101.1 to 118.3° ( $\langle\text{O—Si—O}\rangle$ : 109.4°), respectively. The four independent O atoms are bonded to one Si and three La atoms, resulting in close values of the electrostatic valence. That is not the case for the Yb phase, since the number of bonds with Yb is two for O(1) and O(2), three for O(3) and O(4). This results particularly in an increase of the O(1)—Si—O(2) angle and a decrease of the O(3)—Si—O(4) angle.

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*Acta Cryst.* (1988). **C44**, 1887–1889

## Structure of Dilithium Dimagnesium Trisulfate

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(Received 18 May 1988; accepted 14 June 1988)

**Abstract.**  $\text{Li}_2\text{Mg}_2(\text{SO}_4)_3$ ,  $M_r = 350.69$ , orthorhombic, *Pbcn*,  $a = 12.165$  (2),  $b = 8.538$  (1),  $c = 8.689$  (1) Å,  $V = 902.5$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 2.50$ ,  $D_x = 2.581$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.32$  mm<sup>-1</sup>,  $F(000) = 696$ ,  $T = 293$  K, final  $R = 0.026$  for 1494 reflections. The structure contains almost regular  $\text{SO}_4$  tetrahedra linked by Mg cations which

have distorted octahedral coordination; Li cations are in tetrahedral cavities. This compound, with the small Li cation, belongs to a new family of double sulfates which is structurally different from the langbeinite family stabilized by larger univalent cations.

**Introduction.** The high-temperature form (cubic) of the lithium sulfate  $\text{Li}_2\text{SO}_4$  exhibits high ionic conductivity (Kvist & Lunden, 1965; Benrath & Dreppel, 1921)

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which may be explained by the rotational motion of  $\text{SO}_4$  anions in the crystal (Nillson, Thomas & Tofield, 1980). Many systems with another lithium salt or another sulfate have been studied to obtain a stable solid solution with the  $\text{Li}_2\text{SO}_4$  cubic structure or double sulfates which might be good ionic conductors.

A detailed study of the  $\text{Li}_2\text{SO}_4$ – $\text{MgSO}_4$  equilibrium diagram has been performed recently (Touboul, Le Samedi & Quarton, 1988). An incongruently double sulfate appeared and we have demonstrated that it must be formulated as  $\text{Li}_2\text{Mg}_2(\text{SO}_4)_3$  and not  $\text{Li}_2\text{Mg}_4(\text{SO}_4)_5$  (Liang & Zhang, 1986). The structural determination of this compound, described in this paper, confirms the chemical formulation.

**Experimental.** Single crystals obtained by slow cooling of an  $\text{Li}_2\text{SO}_4$ – $2\text{MgSO}_4$  melt from 1140 K; plate-like crystal was used; crystal dimensions  $0.4 \times 0.2 \times 0.1$  mm;  $D_m$  measured by flotation; systematic absences;  $0kl$  for  $k$  odd,  $h0l$  for  $l$  odd and  $hk0$  for  $h + k$  odd from Weissenberg and oscillation photographs; Syntex  $P2_1$  diffractometer; accurate unit-cell parameters by least-squares refinement of 15 reflections,  $15 < \theta < 45^\circ$ ; intensity data collected with Mo  $K\alpha$  radiation using  $\theta$ – $2\theta$  scanning mode, each reflection scanned  $1^\circ$  ( $2\theta$ ) above and below  $K\alpha$  doublet, background-to-scan-time ratio = 1.0; maximum value of  $(\sin\theta)/\lambda = 0.76 \text{ \AA}^{-1}$ ;  $0 \leq h \leq 18$ ;  $0 \leq k \leq 12$ ;  $0 \leq l \leq 13$ ; three standard reflections (12,0,0, 060 and 008) measured every 96 reflections, no systematic trends; intensities corrected for Lorentz–polarization effects but not for absorption; 1654 unique reflections  $4 \leq \theta \leq 32.5^\circ$ , 1494 with  $I > 2\sigma(I)$  considered observed and included in the refinement; structure solved by direct methods (*MULTAN80*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined anisotropically by full-matrix least squares; in final cycle  $R = 0.026$ ,  $wR = 0.034$  for observed reflections only,  $S = 0.44$ , max. shift/e.s.d. = 0.02; function minimized  $\sum w(\Delta F)^2$ , where  $w = |F_o|/15$  if  $|F_o| < 15$  and  $w = 15/|F_o|$  if  $|F_o| \geq 15$ ; max. and min. heights in final difference Fourier synthesis 0.46 and  $0.55 \text{ e \AA}^{-3}$ ; scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974); all calculations except *MULTAN* with local version of the *NRC* system (Ahmed, Hall, Pippy & Huber, 1973) on a Gould PN 9050 computer. Atomic coordinates are listed in Table 1,\* bond distances and angles in Table 2. A projection of the unit-cell contents down  $\mathbf{b}$  and the numbering of the atoms are shown in Fig. 1.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51148 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates ( $\times 10^5$ ) and equivalent isotropic thermal parameters*

	$B_{\text{eq}} = \frac{4}{3} \sum_i \beta_{ii} a_i^2$			$B_{\text{eq}}(\text{\AA}^2)$
	x	y	z	
Li	67910 (23)	28535 (34)	77911 (30)	1.43
Mg	60926 (4)	24586 (5)	45804 (5)	0.70
S(1)	50000	4719 (4)	75000	0.58
S(2)	64889 (2)	60518 (3)	60478 (3)	0.49
O(1)	57742 (8)	15038 (13)	66711 (12)	1.19
O(2)	56354 (10)	–4633 (14)	85730 (13)	1.52
O(3)	65915 (8)	43325 (11)	60719 (11)	1.02
O(4)	68170 (8)	66642 (11)	75702 (11)	0.92
O(5)	53697 (9)	64993 (13)	56848 (14)	1.44
O(6)	72370 (8)	66920 (13)	48597 (11)	1.10

Table 2. *Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ )*

<b>SO<sub>4</sub> tetrahedra</b>				
S(1)	O(1)	O(1)(i,1)	O(2)	O(2)(i,1)
O(1)	1.477 (1)	2.371 (2)	2.362 (2)	2.410 (2)
O(1)(i,1)	$\frac{106.769 (2)}{107.574 (2)}$	1.477 (1)	2.410 (2)	2.362 (1)
O(2)	107.574 (2)	$\frac{110.774 (4)}{107.574 (2)}$	1.451 (1)	2.422 (2)
O(2)(i,1)	110.774 (4)	107.574 (2)	$\frac{113.205 (4)}{109.173 (5)}$	1.451 (1)
$\langle \text{S(1)–O} \rangle = 1.464$	$\langle \text{O–O} \rangle = 2.390$	$\langle \text{O–S(1)–O} \rangle = 109.45$		
S(2)	O(3)	O(4)	O(5)	O(6)
O(3)	1.473 (1)	2.395 (2)	2.397 (2)	2.405 (2)
O(4)	$\frac{108.482 (4)}{110.208 (5)}$	1.477 (1)	2.409 (2)	2.410 (2)
O(5)	110.208 (5)	$\frac{110.822 (5)}{109.120 (6)}$	1.449 (1)	2.388 (2)
O(6)	109.003 (4)	109.120 (6)	$\frac{109.173 (5)}{109.173 (5)}$	1.481 (1)
$\langle \text{S(2)–O} \rangle = 1.470$	$\langle \text{O–O} \rangle = 2.401$	$\langle \text{O–S(2)–O} \rangle = 109.47$		
<b>LiO<sub>4</sub> tetrahedra</b>				
Li	O(1)	O(3)	O(4)(ii,2)	O(6)(iii,3)
O(1)	1.951 (3)	2.663 (2)	3.036 (2)	3.635 (3)
O(3)	$\frac{85.54 (1)}{100.99 (1)}$	1.971 (3)	3.261 (2)	3.495 (2)
O(4)(ii,2)	100.99 (1)	$\frac{111.08 (1)}{128.00 (4)}$	1.984 (3)	2.693 (2)
O(6)(iii,3)	140.06 (6)	128.00 (4)	$\frac{87.29 (1)}{109.173 (5)}$	1.917 (3)
$\langle \text{Li–O} \rangle = 1.956$	$\langle \text{O–O} \rangle = 3.130$	$\langle \text{O–Li–O} \rangle = 108.83$		
<b>MgO<sub>6</sub> octahedra</b>				
Mg–O(1)	2.028 (1)	Mg–O(4)(iii,3)	2.095 (1)	
O(2)(iii)	1.994 (1)	O(5)(iv,4)	2.002 (1)	
O(3)	2.147 (1)	O(6)(ii,2)	2.149 (1)	
O(1)–Mg–O(2)(iii)	89.801 (7)	O(2)(iii)–Mg–O(4)(iii,3)	93.254 (4)	
O(3)	79.213 (5)	O(5)(iv,4)	94.663 (5)	
O(5)(iv,4)	96.431 (7)	O(6)(ii,2)	93.044 (5)	
O(6)(ii,2)	87.536 (7)	O(3)–Mg–O(4)(iii,3)	96.775 (4)	
O(4)(iii,3)–Mg–O(5)(iv,4)	96.829 (6)	O(5)(iv,4)	89.397 (5)	
O(6)(ii,2)	78.769 (4)	O(6)(ii,2)	83.769 (4)	
O(1)–Mg–O(4)(iii,3)	166.10 (8)	$\langle \text{Mg–O} \rangle = 2.069$		
O(2)(iii)–Mg–O(3)	168.67 (11)	$\langle \text{O–O} \rangle = 2.920$		
O(5)(iv,4)–Mg–O(6)(ii,2)	171.34 (14)	$\langle \text{O–Mg–O} \rangle = 89.96$		

Symmetry codes: (i):  $x, y, z$ ; (ii):  $\bar{x}, y, \frac{1}{2}-z$ ; (iii):  $\frac{1}{2}-x, \frac{1}{2}+y, z$ ; (iv):  $x, \bar{y}, \frac{1}{2}+z$ ; (v):  $\bar{x}, \bar{y}, \bar{z}$ ; (1): 101; (2): 100; (3): 010; (4): 111.

**Discussion.** All the atoms are in 8(*d*) general positions except S(1) which is in 4(*c*) special position.  $\text{SO}_4$  tetrahedra are almost regular; on the other hand,  $\text{LiO}_4$  tetrahedra are very irregular and  $\text{MgO}_6$  octahedra slightly less so. However, the average bonds (Table 2) are very close to the sum of ionic radii (Shannon, 1976):  $r_{\text{S}^{6+}} + r_{\text{O}^{2-}} = 1.47$ ;  $r_{\text{Li}^+} + r_{\text{O}^{2-}} = 1.95$  and  $r_{\text{Mg}^{2+}} + r_{\text{O}^{2-}} = 2.07 \text{ \AA}$ .

The structure contains chains of polyhedra along the  $\mathbf{c}$  direction. Each chain, in zigzag, consists of  $\text{LiO}_4$  and  $\text{MgO}_6$  polyhedra linked together by vertices (left side of Fig. 1). Each of these chains is developed around  $2_1$  axes parallel to the  $z$  axis. These  $[\text{LiMgO}_6]_\infty$  chains are linked together by  $\text{SO}_4$  tetrahedra. Thus, each S(1) $\text{O}_4$

tetrahedron connects four chains while each  $S(2)O_4$  tetrahedron connects three chains only, because one of its edges [O(4)–O(6)] associates two anions of the same chain (left side of Fig. 1). It results that the coordination of O(1), O(3), O(4) and O(6) is three ( $Li^+$ ,  $Mg^{2+}$  and  $S^{6+}$ ) and the coordination of O(2) and O(5) is two ( $Mg^{2+}$  and  $S^{6+}$ ). Consequently, Mg–O(2) and Mg–O(5) are the shortest Mg–O bonds like S(1)–O(2) and S(2)–O(5) among S–O bonds (Table 2).

The structure may also be described as a set of isolated  $SO_4$  tetrahedra surrounded by Mg cations which have distorted octahedral coordinations; Li cations are in tetrahedral cavities (right side of Fig. 1).

The structure of  $Li_2Mg_2(SO_4)_3$  is close to those of  $LiLu(SO_4)_2$  and  $Er_2(SO_4)_3$  (Sirovkin, Pokrovskij & Kovba, 1981). These two compounds crystallize with the same space group (*Pbcn*) and  $Z=6$  and 4 respectively. The cells of these three structures contain the same number of O and S atoms, almost on the same positions. Mg, Er and ( $\frac{3}{4}Lu + \frac{1}{4}Li$ ) cations have the same positions with distorted octahedral coordinations. The difference between these structures proceeds from the Li cations; there is no Li in  $Er_2(SO_4)_3$  and in  $LiLu(SO_4)_2$  two-thirds of the six Li cations occupy the 4(a) position (0,0,0.5) with a very distorted tetrahedral coordination. The S–O distances are very similar in the double salts  $LiLu(SO_4)_2$  (1.456 and 1.439 Å) and  $Li_2Mg_2(SO_4)_3$  (Table 2), but in the octahedra Lu–O distances vary from 2.167 to 2.237 Å and Mg–O

distances from 1.994 to 2.149 Å according to the values of the ionic radii (Shannon, 1976):  $r_{Lu^{3+}} = 0.86$ ,  $r_{Mg^{2+}} = 0.72$  Å. However, the major differences are in the Li–O bonds which are 1.770 and 2.168 Å in  $LiLu(SO_4)_2$  although the average Li–O distance is 1.969 Å, a value which is very close to that found in  $Li_2Mg_2(SO_4)_3$  (Table 2). So  $Li_2Mg_2(SO_4)_3$  and  $LiLu(SO_4)_2$  are almost isostructural compounds, although their chemical formulae are different. The atomic arrangement of  $Er_2(SO_4)_3$  constitutes the chief structure where some kinds of vacant tetrahedral cavities exist; these cavities can receive small Li cations only. With  $Li_2Mn_2(SO_4)_3$ , a compound isotypic with  $Li_2Mg_2(SO_4)_3$  (Touboul *et al.*, 1988), it appears that a new structural type of double sulfates has been characterized, associated with the  $Er_2(SO_4)_3$  structure. This new structural type is different from the langbeinite structure adopted by another double-sulfate family (Mereiter, 1979; Zemmann & Zemmann, 1957). Langbeinite-type compounds are also formulated as  $M_2^I M_2^{II}(SO_4)_3$ , with the same bivalent cations ( $M^{II} = Mg, Mn$ ) as  $Li_2M_2^{II}(SO_4)_3$ , but exclusively with univalent cations ( $M^I = K^+, Rb^+, Cs^+, Tl^+, NH_4^+$ ) larger than Li.

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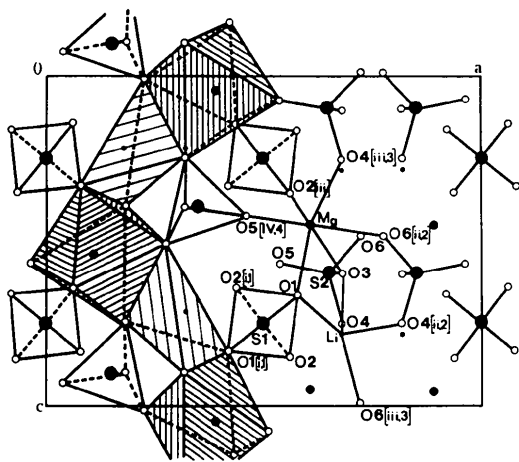


Fig. 1. Projection of the unit-cell contents down *b* (see text).