

Cr and Na atoms, can be seen in Fig. 1. The two  $\text{CrO}_4$  tetrahedra, inside each unit cell, are disposed with their apices in opposite directions along the  $c$  axis (Figs. 1 and 2). This kind of packing is the same as that of the isomorphous compound  $\text{K}_3\text{Na}(\text{SO}_4)_2$  (Okada & Ossaka, 1980).

The Na—O distances in the  $\text{NaO}_6$  octahedron are symmetry restricted to a single value of 2.364 Å. The mean distances in the  $\text{K}(1)\text{O}_{10}$  and  $\text{K}(2)\text{O}_{12}$  polyhedra are 2.969 and 3.155 Å respectively.

The Cr—O distances range from 1.613 to 1.6459 Å with a mean value of 1.639 Å. The values of the two possible bond angles O—Cr—O, in the  $\text{CrO}_4$  group (110.31 and 108.63°), indicate a very small distortion with respect to the ideal tetrahedral configuration. The rigidity of this group was revealed by means of a librational thermal-motion analysis based on the anisotropic atomic displacement parameters of the Cr, O(1) and O(2) atoms. The results show that the thermal motion of the  $\text{CrO}_4$  groups can be completely described by the **T** and **L** tensors (Schomaker & Trueblood, 1968). The residual deformation deduced from the comparison between the observed and calculated atomic displacement parameters is practically zero for this tetrahedron. The corrected bond lengths involving Cr—O(1) and Cr—O(2) atom pairs (see Table 2) exhibit, therefore, closer values (1.646 and 1.661 Å respectively).

The elastic stiffness tensor component  $C_{44}$  shows a usual decrease with increasing temperature from about 250 K up to room temperature. Below 250 K, in the vicinity of the phase transition, the  $C_{44}$  component strongly decreases and acoustic phonon softening is quite evident (Gómez-Cuevas & Breczewski, 1990). The strong damping of ultrasound waves by the ferroelastic domain walls prevents measurement below the phase transition.

In the present case, the softening of  $C_{44}$  is necessary only for the appearance of  $2/m$  symmetry in the ferroelastic phase (Toledano, Fejer & Auld, 1983). In

fact, such a symmetry change, as probed by ultrasonic measurements, would also require similar behaviour in  $C_{11}$ – $C_{12}$  (equal to  $2 \times C_{66}$  for this point group) at the transition temperature. Unfortunately, the morphology of the samples hindered the study of  $C_{11}$ – $C_{12}$  as a function of temperature.

Nevertheless, previous results published by Krajewski, Mroz, Piskunowicz & Breczewski (1990) concerning the domain structure of the ferroelectric phase, together with the X-ray measurements presented above and the behaviour of the elastic tensor component  $C_{44}$  confirm, as expected from Landau theory (Toledano, Fejer & Auld, 1983; Sapriel, 1975), the change of point symmetry in the phase transition from  $\bar{3}m$  to  $2/m$ .

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#### References

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.  
 GÓMEZ-CUEVAS, A. & BRECZEWSKI, T. (1990). In preparation.  
 KRAJEWSKI, T., MROZ, B., PISKUNOWICZ, P. & BRECZEWSKI, T. (1990). *Ferroelectrics*. In the press.  
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO78*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.  
 OKADA, K. & OSSAKA, J. (1980). *Acta Cryst.* **B36**, 919–921.  
 SAPRIEL, J. (1975). *Phys. Rev. B*, **12**, 5128–5140.  
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.  
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The *XRAY* system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.  
 TOLEDANO, P., FEJER, M. M. & AULD, B. A. (1983). *Phys. Rev. B*, **27**, 5717–5746.

*Acta Cryst.* (1990). **C46**, 2021–2026

## Structure of $\text{Li}_4\text{Ge}_5\text{O}_{12}$ – a New Compound in the $\text{Li}_2\text{O}$ – $\text{GeO}_2$ System

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**Abstract.** Tetralithium pentagermanate  $\text{Li}_4\text{Ge}_5\text{O}_{12}$ ,  $M_r = 582.7$ , triclinic,  $P\bar{1}$ ,  $a = 5.120$  (1),  $b = 9.143$  (2),  $c = 9.586$  (2) Å,  $\alpha = 72.95$  (3),  $\beta = 77.74$  (3),  $\gamma =$

$78.81$  (3)°,  $V = 415.02$  (15) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 4.63$ ,  $D_x = 4.663$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 17.74$  mm<sup>-1</sup>,  $F(000) = 536$ ,  $T = 295$  (2) K,  $R =$

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0.025 for 1334 independent observed reflections. The structure consists of quasi-close-packed planes of O atoms held together by Ge and Li cations. Two of the five Ge in the asymmetric unit are tetrahedrally coordinated with  $\langle \text{Ge}-\text{O} \rangle = 1.748$  (21) Å and the other three are octahedrally coordinated with  $\langle \text{Ge}-\text{O} \rangle = 1.901$  (59) Å. Crystals up to 1.5 cm in diameter and 4.0 cm in length were pulled from a melt of composition  $3\text{Li}_2\text{O} \cdot 0.8\text{GeO}_2$  at 1208 (5) K.

**Introduction.** Recently, optical studies of a  $\text{Ti}^{4+}$ -activated lithium germanium oxide compound were reported (Loiacono, Shone, Mizell, Powell, Quarles & Elouadi, 1986). The composition of the host crystal was thought to be ' $\text{Li}_6\text{Ge}_8\text{O}_{19}$ '. This was based on the phase diagram of Murthy & Ip (1964) who reported a congruently melting phase of this composition. Subsequent studies show that under the growth conditions described below, crystals of composition  $\text{Li}_4\text{Ge}_5\text{O}_{12}$  grow from a melt of composition  $\text{Li}_6\text{Ge}_8\text{O}_{19}$ .  $\text{Li}_4\text{Ge}_5\text{O}_{12}$  is a new crystalline phase in the  $\text{Li}_2\text{O}-\text{GeO}_2$  system.

The  $\text{Li}_2\text{O}-\text{GeO}_2$  system has been reported by Murthy & Ip (1964) to contain five congruently melting compounds. These are listed in Table 1 along with other compounds that have been isolated as single crystals. Of the five congruently melting phases, four have been isolated and studied as single crystals. These are:  $\text{Li}_4\text{GeO}_4$ ,  $\text{Li}_6\text{Ge}_2\text{O}_7$ ,  $\text{Li}_2\text{GeO}_3$  and  $\text{Li}_2\text{Ge}_7\text{O}_{15}$ . Some doubt has been expressed about the existence of ' $\text{Li}_6\text{Ge}_8\text{O}_{19}$ ' (Wittman & Modern, 1965; Ikeda & Sato, 1984). This doubt is supported by our observation that 24 of the first 25 X-ray powder-diffraction lines listed by Murthy & Ip (1964) as characteristic of ' $\text{Li}_6\text{Ge}_8\text{O}_{19}$ ' correspond quite closely to lines from  $\text{Li}_4\text{Ge}_5\text{O}_{12}$  (given in Table 2), and/or  $\text{Li}_2\text{GeO}_3$  (JCPDS No. 34-6590), and/or  $\text{Li}_2\text{Ge}_4\text{O}_9$  (JCPDS No. 37-1363), and/or  $\text{Li}_2\text{Ge}_7\text{O}_{15}$  (JCPDS No. 23-1180) (*Powder Diffraction File*, JCPDS International Centre for Diffraction Data, Swarthmore, Pennsylvania, USA).

## Experimental.

### Crystal growth

The initial intent of these experiments was to grow crystals of composition ' $\text{Li}_6\text{Ge}_8\text{O}_{19}$ '. Such crystals would contain 90.32 wt %  $\text{GeO}_2$ . With that goal in mind the procedure described below was used and large single crystals were obtained. These crystals were later shown by an X-ray single-crystal structure determination to be  $\text{Li}_4\text{Ge}_5\text{O}_{12}$  which contains 89.75 wt %  $\text{GeO}_2$ .

Crystal growth of  $\text{Li}_4\text{Ge}_5\text{O}_{12}$  proceeded as follows. AESAR, 99.99% pure  $\text{Li}_2\text{CO}_3$  and hexagonal  $\text{GeO}_2$  were the starting materials. These were mixed in the molar ratio 3:8, ball milled using an alumina con-

Table 1. *Li-Ge-O phases reported to be congruently melting by Murthy & Ip (1964) and phases for which single-crystal structure determinations have been made*

Phase	Ratio of $\text{Li}_2\text{O}:\text{GeO}_2$	Wt % $\text{GeO}_2$	Congruently melting	Space group	Structure reference
$\text{Li}_4\text{GeO}_4$	2:1	63.64	Yes	<i>Bmmb</i>	Vollenkle & Wittman (1969)
$\text{Li}_6\text{Ge}_2\text{O}_7$	3:2	70.00	Yes	<i>P2_1/n</i>	Vollenkle (1980)
$\text{Li}_2\text{GeO}_3$	1:1	77.78	Yes	<i>Cmc2_1</i>	Vollenkle & Wittman (1968a)
$\text{Li}_2\text{Ge}_2\text{O}_3$	1:2	87.50	No	<i>Cc</i>	Vollenkle & Wittman (1968b)
$\text{Li}_4\text{Ge}_5\text{O}_{12}$	2:5	89.75	No	<i>P1</i>	This work
( $\text{Li}_6\text{Ge}_8\text{O}_{19}$ )	3:8	90.32	(Yes)	—	—
$\text{Li}_2\text{Ge}_4\text{O}_9$	1:4	93.33	No	<i>Pcca</i>	Wittman & Modern (1965)
$\text{Li}_4\text{Ge}_9\text{O}_{20}$	2:9	94.03	No	<i>C2</i>	Vollenkle & Wittman (1971)
$\text{Li}_2\text{Ge}_7\text{O}_{15}$	1:7	96.08	Yes	<i>Pbcn</i>	Vollenkle & Wittman (1970)

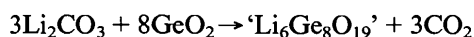
It is doubtful that the phase labeled  $\text{Li}_6\text{Ge}_8\text{O}_{19}$  exists.

Table 2. *X-ray powder-diffraction data for  $\text{Li}_4\text{Ge}_5\text{O}_{12}$*

Pearson symbol *TP2*. Philips 17 cm vertical diffractometer used with  $\text{Cu } K\alpha$  radiation,  $\lambda = 1.54060$  Å, adjustable divergence slit maintaining a 12.5 mm sample illumination length, 0.2 mm rec. slit, 1 Soller slit, graphite diffracted-beam monochromator, scintillation detector and instrumental profile breadth of  $0.10^\circ$ . Data were collected at 295 K from a thin sample with particle size  $< 325$  mesh. Intensities were measured as peak heights from  $0.02^\circ$  step scans and a Si external  $2\theta$  standard was used.

$2\theta_{\text{exp}} (^\circ)$	$I/I_0$	<i>d</i>	<i>hkl</i>
9.79	22	9.03	001
10.21	2	8.65	010
15.91	7	5.56	01
17.88	5	4.96	100
18.92	82	4.69	101, 111
19.33	26	4.59	110
19.63	100	4.521	012, 002
20.27	12	4.379	021
20.50	5	4.330	020
21.84	21	4.065	10
23.87	12	3.724	11, 121
24.46	3	3.637	022, 02
25.00	7	3.559	021
25.33	18	3.514	120
28.67	85	3.111	013
29.21	8	3.055	120
29.61	59	3.015	003
30.06	12	2.970	12
30.15	10	2.962	12
31.36	6	2.850	023
31.67	8	2.823	121, 131
32.09	40	2.787	103, 032
32.86	7	2.723	132
33.64	1	2.662	130
33.99	4	2.635	013, 122

tainer and balls, then calcined in air. The calcination sequence was 873 K for 17 h then 1073 K for 17 h and finally 1173 K for 17 h. The material was ball milled between firings and pure platinum crucibles were used for all calcinations and for subsequent crystal growth. Weight-loss measurements showed the amount of  $\text{CO}_2$  evolved after the 1173 K firing corresponded to the reaction



It was from this material that large single crystals were grown using the Czochralski method and a resistance furnace. The growth temperature was maintained at 1208 (5) K and the temperature gradient of the melt/air interface was controlled to  $10 \text{ K cm}^{-1}$ . Crystals were pulled in air at rates from  $0.1$  to  $5 \text{ mm h}^{-1}$  with rotation rates of  $5$  to  $50 \text{ rev min}^{-1}$ . Best results were obtained at  $1 \text{ mm h}^{-1}$  and  $25 \text{ rev min}^{-1}$  from melt volumes of  $100 \text{ cm}^3$  and yielded single-crystal boules  $1.5 \text{ cm}$  in diameter and  $4.0 \text{ cm}$  in length. Fig. 1 shows one such crystal. Grown crystals were cooled to room temperature at  $50 \text{ K h}^{-1}$ .

Concentrations of  $\text{Ti}^{4+}$  from  $0.01$  to  $0.3 \text{ wt } \%$  could be incorporated in the  $\text{Li}_4\text{Ge}_5\text{O}_{12}$  without a change in the appearance of the crystals when examined with an optical microscope. These crystals exhibited broad-band luminescence from  $388$  to  $524 \text{ nm}$  when excited with  $266 \text{ nm}$  radiation (Loiacono *et al.*, 1986).

#### Crystal structure determination

The composition and crystal structure of  $\text{Li}_4\text{Ge}_5\text{O}_{12}$  were determined from room-temperature X-ray diffraction measurements of a  $0.35 \text{ mm}$  spherical crystal using a Nicolet single-crystal diffractometer. Variable speed  $\omega$  scans were made of reflections in the  $2\theta$  range  $3$ – $50^\circ$  ( $|h| \leq 6$ ,  $|k| \leq 10$ ,  $|l| \leq 11$ ) using graphite-monochromated  $\text{Mo K}\alpha$  radiation. Two standard reflections were measured after every 48 reflections. These showed a random variation in intensity of  $\pm 1.7\%$  with time. Twenty five reflections in the  $2\theta$  range  $9$ – $28^\circ$  were used to establish the lattice parameters. The measured

density was determined by weighing and measuring the dimensions of a rectangular, single-crystal parallelepiped.

The crystal structure was solved by direct methods using the random tangent refinement procedures, *RANT* in the *SHELXTL-Plus* software package (Sheldrick, 1987). 2918 reflections were measured, 1459 were independent ( $R_{\text{int}} = 2.12\%$ ) and 1334 were observed [*i.e.*  $F > 4.0\sigma(F)$ ]. A full-matrix least-squares refinement was carried out minimizing the quantity  $\sum w(F_o - F_c)^2$  and employing the weighting scheme  $w^{-1} = \sigma^2(F) + 0.001F^2$  where  $\sigma(F)$  is based on counting statistics. Refinements of  $F_c$  were made by varying 191 structural parameters including anisotropic Ge temperature factors, an overall scale factor and an extinction parameter,  $x$ , which refined to  $0.0081(4)$  where  $F^* = F[1 + 0.002xF^2/\sin(2\theta)]^{-1/4}$ . No absorption correction was applied. Results of the refinement for observed  $F$ 's are:  $R = 2.51\%$ ,  $wR = 3.69\%$ ; and for all  $F$ 's:  $R = 2.68\%$ ,  $wR = 4.72\%$ . The largest mean  $\Delta/\sigma = 0.007$ , the largest difference peak is  $0.77 \text{ e } \text{\AA}^{-3}$  and the largest difference hole is  $0.74 \text{ e } \text{\AA}^{-3}$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) were used with anomalous-dispersion corrections for Ge and O.

**Discussion.** Final atomic positions and equivalent isotropic thermal parameters are given in Tables 3 and 4† and indicate that the structure is centrosymmetric,  $P\bar{1}$ . Consistent with this symmetry, no optical second harmonic signal could be measured using an apparatus sensitive to a signal equal to  $10^{-3} \times \alpha$  quartz (Dougherty & Kurtz, 1976). The structure consists of quasi-close-packed planes of O anions held together by Li and Ge cations. These oxygen planes lie very close to the  $ab^*$  plane of the crystal and are stacked in an f.c.c. sequence. The planar arrangement of O atoms can clearly be seen in Fig. 2 which shows the structure as viewed along the  $a$  axis. The structure can also be considered in terms of Ge–O coordination polyhedra which may be linked at corners and/or along edges. The packing of these polyhedra is illustrated in Fig. 3 which is also a view along the  $a$  axis.

Four of the ten Ge per unit cell are in tetrahedral coordination and the other six in octahedral coordination. Taken together the tetrahedra have  $\langle \text{Ge—O} \rangle = 1.748(21) \text{ \AA}$ ,  $1.723 < \text{Ge—O} < 1.778 \text{ \AA}$  and  $103.8 < \text{O—Ge—O} < 113.8^\circ$ . Each tetrahedron is corner linked to one other tetrahedron in the unit cell.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53094 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

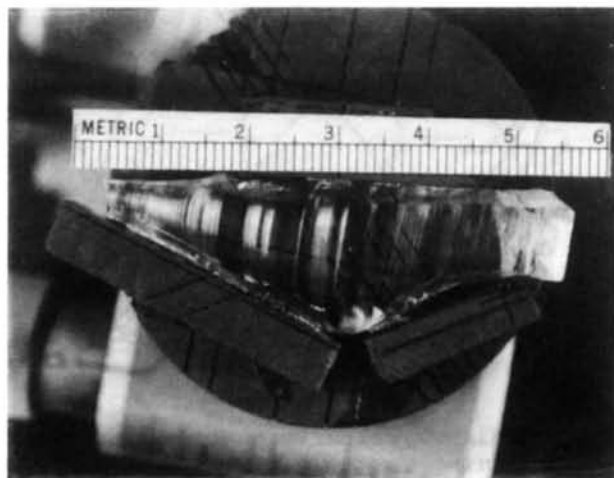


Fig. 1. Single crystal of  $\text{Li}_4\text{Ge}_5\text{O}_{12}$  grown at  $1208(5) \text{ K}$  by the Czochralski technique using a resistance-heated furnace. The crystal is shown mounted for fabrication. The growth direction, parallel to the ruler, is close to the crystal  $a$  axis.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement coefficients

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$ (Å <sup>2</sup> )
Ge(1)	0.1890 (1)	0.2539 (1)	0.9353 (1)	0.013 (1)
Ge(2)	0.1907 (1)	0.0998 (1)	0.6822 (1)	0.013 (1)
Ge(3)	0.4092 (1)	0.4206 (1)	0.6452 (1)	0.013 (1)
Ge(4)	0.2614 (1)	0.0969 (1)	1.2683 (1)	0.013 (1)
Ge(5)	0.1179 (1)	0.5943 (1)	0.8511 (1)	0.013 (1)
O(1)	0.2674 (8)	0.5665 (4)	0.4843 (4)	0.017 (1)
O(2)	0.3191 (8)	0.2631 (4)	0.5689 (4)	0.017 (1)
O(3)	0.4431 (8)	0.5791 (4)	0.7304 (4)	0.018 (1)
O(4)	0.0543 (8)	0.4309 (4)	0.7757 (4)	0.015 (1)
O(5)	-0.0511 (8)	0.7395 (4)	0.6994 (4)	0.016 (1)
O(6)	0.5120 (8)	0.2704 (4)	0.8102 (4)	0.017 (1)
O(7)	0.2308 (8)	0.4232 (4)	1.0126 (4)	0.016 (1)
O(8)	0.1475 (8)	0.7322 (4)	0.9509 (4)	0.015 (1)
O(9)	0.4372 (7)	-0.0618 (4)	0.6613 (4)	0.015 (1)
O(10)	0.1025 (7)	0.1015 (4)	0.8664 (4)	0.016 (1)
O(11)	0.3458 (7)	0.1008 (4)	1.0816 (4)	0.017 (1)
O(12)	-0.0926 (8)	0.0639 (4)	0.6286 (4)	0.016 (1)
Li(1)	0.6486 (19)	0.4234 (11)	0.8895 (10)	0.024 (4)
Li(2)	0.1428 (22)	0.4071 (12)	0.4036 (10)	0.027 (4)
Li(3)	-0.2748 (19)	0.0968 (10)	0.9765 (10)	0.022 (3)
Li(4)	0.3107 (22)	0.7708 (12)	0.5557 (12)	0.030 (4)

Table 4. Selected bond lengths (Å) and angles (°) for  $Li_4Ge_5O_{12}$ 

Ge(1)—O(4)	2.000 (4)	Li(1)—O(3)	2.070 (10)
Ge(1)—O(6)	1.829 (4)	Li(1)—O(4A)	2.135 (9)
Ge(1)—O(7)	1.965 (5)	Li(1)—O(6)	2.062 (13)
Ge(1)—O(8A)	1.837 (4)	Li(1)—O(7B)	2.141 (13)
Ge(1)—O(10)	1.865 (5)	Li(1)—O(7)	2.213 (9)
Ge(1)—O(11)	1.861 (4)	Li(1)—O(8B)	2.069 (10)
Ge(2)—O(2)	1.723 (4)	Li(2)—O(1)	2.089 (14)
Ge(2)—O(9)	1.777 (4)	Li(2)—O(1B)	2.150 (11)
Ge(2)—O(10)	1.732 (4)	Li(2)—O(2)	1.995 (10)
Ge(2)—O(12)	1.754 (5)	Li(2)—O(3A)	2.239 (11)
Ge(3)—O(1)	1.891 (4)	Li(2)—O(4B)	2.197 (10)
Ge(3)—O(1A)	1.848 (4)	Li(2)—O(5B)	2.051 (14)
Ge(3)—O(2)	1.960 (5)	Li(3)—O(6A)	2.199 (9)
Ge(3)—O(3)	1.911 (5)	Li(3)—O(8A)	2.139 (12)
Ge(3)—O(4)	1.978 (4)	Li(3)—O(10)	1.997 (9)
Ge(3)—O(6)	1.861 (4)	Li(3)—O(10A)	2.162 (9)
Ge(4)—O(5A)	1.732 (4)	Li(3)—O(11A)	1.988 (10)
Ge(4)—O(9B)	1.750 (4)	Li(3)—O(11B)	2.154 (12)
Ge(4)—O(11)	1.741 (4)	Li(4)—O(1)	2.232 (14)
Ge(4)—O(12A)	1.778 (4)	Li(4)—O(2A)	2.036 (11)
Ge(5)—O(3)	1.821 (4)	Li(4)—O(3)	2.153 (11)
Ge(5)—O(4)	1.945 (5)	Li(4)—O(5)	2.074 (11)
Ge(5)—O(5)	1.893 (4)	Li(4)—O(9A)	2.315 (15)
Ge(5)—O(7)	1.946 (4)	Li(4)—O(12B)	2.296 (11)
Ge(5)—O(7A)	1.979 (4)		
Ge(5)—O(8)	1.836 (5)		
O(4)—Ge(1)—O(6)	83.1 (4)	O(3)—Li(1)—O(4A)	100.1 (4)
O(4)—Ge(1)—O(7)	81.7 (2)	O(3)—Li(1)—O(7B)	101.0 (4)
O(4)—Ge(1)—O(10)	95.2 (2)	O(3)—Li(1)—O(8B)	179.8 (5)
O(4)—Ge(1)—O(11)	173.7 (2)	O(6)—Li(1)—O(7)	79.0 (4)
O(4)—Ge(1)—O(8A)	89.6 (2)	O(6)—Li(1)—O(4A)	103.6 (5)
O(6)—Ge(1)—O(7)	91.6 (2)	O(6)—Li(1)—O(7B)	175.6 (5)
O(6)—Ge(1)—O(10)	94.6 (2)	O(6)—Li(1)—O(8B)	99.4 (4)
O(6)—Ge(1)—O(11)	92.5 (2)	O(7)—Li(1)—O(4A)	177.4 (7)
O(6)—Ge(1)—O(8A)	171.6 (2)	O(7)—Li(1)—O(7B)	97.1 (4)
O(7)—Ge(1)—O(10)	172.7 (2)	O(7)—Li(1)—O(8B)	99.6 (4)
O(7)—Ge(1)—O(11)	93.9 (2)	O(4A)—Li(1)—O(7B)	80.3 (4)
O(7)—Ge(1)—O(8A)	83.2 (2)	O(4A)—Li(1)—O(8B)	80.1 (3)
O(10)—Ge(1)—O(11)	89.6 (2)	O(7B)—Li(1)—O(8B)	79.0 (4)
O(10)—Ge(1)—O(8A)	90.2 (2)	O(1)—Li(2)—O(2)	80.1 (5)
O(11)—Ge(1)—O(8A)	94.4 (2)	O(1)—Li(2)—O(1B)	95.2 (5)
O(2)—Ge(2)—O(9)	107.5 (2)	O(1)—Li(2)—O(3A)	80.0 (4)
O(2)—Ge(2)—O(10)	113.8 (2)	O(1)—Li(2)—O(4B)	99.0 (4)

Table 4 (cont.)

O(2)—Ge(2)—O(12)	113.5 (2)	O(1)—Li(2)—O(5B)	173.0 (5)
O(9)—Ge(2)—O(10)	110.7 (2)	O(2)—Li(2)—O(1B)	99.9 (4)
O(9)—Ge(2)—O(12)	103.8 (2)	O(2)—Li(2)—O(3A)	87.3 (4)
O(10)—Ge(2)—O(12)	107.2 (2)	O(2)—Li(2)—O(4B)	178.8 (7)
O(1)—Ge(3)—O(2)	86.1 (2)	O(2)—Li(2)—O(5B)	103.1 (5)
O(1)—Ge(3)—O(3)	92.1 (2)	O(1B)—Li(2)—O(3A)	170.7 (5)
O(1)—Ge(3)—O(4)	91.8 (2)	O(1B)—Li(2)—O(4B)	79.5 (4)
O(1)—Ge(3)—O(6)	173.8 (2)	O(1B)—Li(2)—O(5B)	90.4 (5)
O(1)—Ge(3)—O(1A)	83.6 (2)	O(3A)—Li(2)—O(4B)	93.3 (4)
O(2)—Ge(3)—O(3)	171.8 (2)	O(3A)—Li(2)—O(5B)	93.8 (4)
O(2)—Ge(3)—O(4)	91.5 (2)	O(4B)—Li(2)—O(5B)	77.9 (4)
O(2)—Ge(3)—O(6)	90.9 (2)	O(10)—Li(3)—O(6A)	99.1 (4)
O(2)—Ge(3)—O(1A)	92.1 (2)	O(10)—Li(3)—O(8A)	78.6 (4)
O(3)—Ge(3)—O(4)	80.5 (2)	O(10)—Li(3)—O(10A)	85.1 (4)
O(3)—Ge(3)—O(6)	90.2 (2)	O(10)—Li(3)—O(11A)	177.7 (5)
O(3)—Ge(3)—O(1A)	95.6 (2)	O(10)—Li(3)—O(11B)	96.2 (4)
O(4)—Ge(3)—O(6)	82.9 (2)	O(6A)—Li(3)—O(8A)	93.2 (4)
O(4)—Ge(3)—O(1A)	173.9 (2)	O(6A)—Li(3)—O(10A)	170.2 (6)
O(6)—Ge(3)—O(1A)	101.9 (2)	O(6A)—Li(3)—O(11A)	78.9 (3)
O(11)—Ge(4)—O(5A)	113.3 (2)	O(6A)—Li(3)—O(11B)	95.7 (5)
O(11)—Ge(4)—O(9B)	107.5 (2)	O(8A)—Li(3)—O(10A)	96.4 (5)
O(11)—Ge(4)—O(12A)	111.3 (2)	O(8A)—Li(3)—O(11A)	100.4 (4)
O(5A)—Ge(4)—O(9B)	113.4 (2)	O(8A)—Li(3)—O(11B)	170.3 (5)
O(5A)—Ge(4)—O(12A)	106.8 (2)	O(10A)—Li(3)—O(11A)	97.0 (4)
O(9B)—Ge(4)—O(12A)	104.3 (2)	O(10A)—Li(3)—O(11B)	74.9 (3)
O(3)—Ge(5)—O(4)	83.7 (2)	O(11A)—Li(3)—O(11B)	85.1 (4)
O(3)—Ge(5)—O(5)	93.0 (2)	O(1)—Li(4)—O(3)	77.2 (4)
O(3)—Ge(5)—O(7)	94.2 (2)	O(1)—Li(4)—O(5)	87.6 (5)
O(3)—Ge(5)—O(8)	103.7 (2)	O(1)—Li(4)—O(2A)	79.9 (4)
O(3)—Ge(5)—O(7A)	171.4 (2)	O(1)—Li(4)—O(9A)	165.4 (6)
O(4)—Ge(5)—O(5)	88.3 (2)	O(1)—Li(4)—O(12B)	91.3 (5)
O(4)—Ge(5)—O(7)	83.7 (2)	O(3)—Li(4)—O(5)	79.2 (4)
O(4)—Ge(5)—O(8)	170.7 (2)	O(3)—Li(4)—O(2A)	88.6 (4)
O(4)—Ge(5)—O(7A)	89.3 (2)	O(3)—Li(4)—O(9A)	89.5 (5)
O(5)—Ge(5)—O(7)	168.6 (2)	O(3)—Li(4)—O(12B)	165.6 (7)
O(5)—Ge(5)—O(8)	96.7 (2)	O(5)—Li(4)—O(2A)	164.2 (6)
O(5)—Ge(5)—O(7A)	91.7 (2)	O(5)—Li(4)—O(9A)	96.1 (5)
O(7)—Ge(5)—O(8)	90.1 (2)	O(5)—Li(4)—O(12B)	91.8 (4)
O(7)—Ge(5)—O(7A)	80.0 (2)	O(2A)—Li(4)—O(9A)	93.9 (5)
O(8)—Ge(5)—O(7A)	82.9 (2)	O(2A)—Li(4)—O(12B)	98.0 (4)
O(3)—Li(1)—O(6)	80.6 (4)	O(9A)—Li(4)—O(12B)	102.7 (4)
O(3)—Li(1)—O(7)	80.2 (3)		

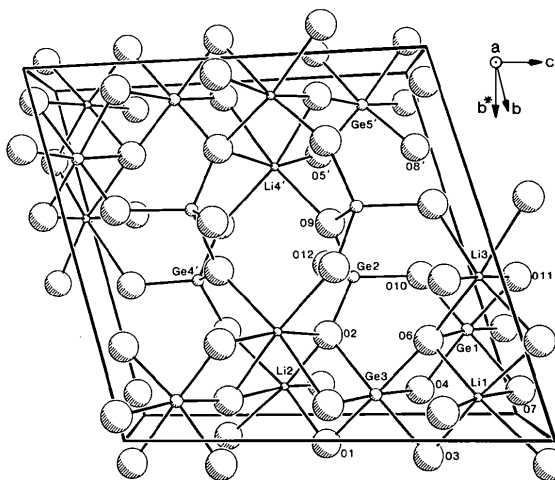


Fig. 2. The  $Li_4Ge_5O_{12}$  structure viewed along the *a* axis. Oxygen anions lie in quasi-close-packed planes parallel to the  $ab^*$  plane of the crystal. A center of symmetry is located at the center of the unit cell which is taken as the origin for labeling the atoms. Atoms labeled  $Li4^*$ ,  $Ge5^*$ ,  $O5^*$  and  $O8^*$  have coordinates given in Table 3 minus '*b*'.  $Ge4^*$  has the coordinates of Table 3 minus '*c*'.

These linked pairs join with like pairs in adjacent cells to form chains that run along the  $a$  axis of the crystal. Taken together the octahedra have  $\langle \text{Ge—O} \rangle = 1.901$  (51) Å,  $1.821 < \text{Ge—O} < 2.000$  Å and  $\text{O—Ge—O} \geq 80.0^\circ$ . The octahedra are edge linked to one another and lie in zigzag bands perpendicular to  $a$  and  $b^*$ . Each of the eight Li per unit cell is surrounded by an irregular oxygen octahedron. Overall  $\langle \text{Li—O} \rangle = 2.132$  (91) Å,  $1.988 < \text{Li—O} < 2.315$  Å and  $\text{O—Li—O} \geq 74.9^\circ$ . Four of the eight lithium per unit cell lie in rectangular channels that lie along the  $a$  axis of the crystal.

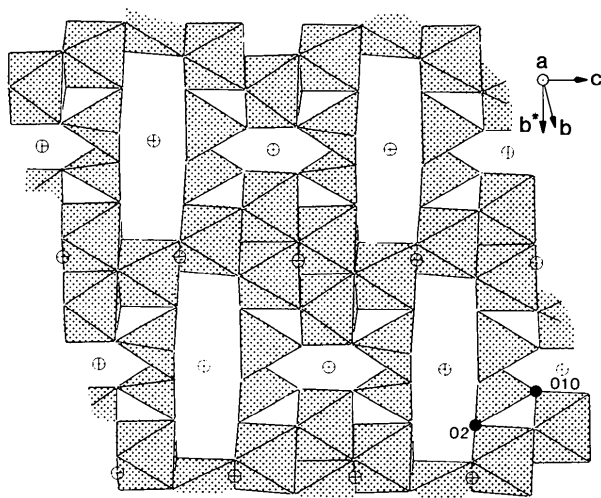


Fig. 3. Packing arrangement of Ge—O polyhedra in  $\text{Li}_4\text{Ge}_5\text{O}_{12}$  viewed along the crystal  $a$  axis. Shaded triangles show corner-linked Ge—O tetrahedra that run in chains along the  $a$  axis. Shaded rectangles show edge-linked Ge—O octahedra that lie in bands perpendicular to  $a$  and  $b^*$ . Four of the eight Li per unit cell lie in the open rectangular channels that lie along  $a$ . Centers of symmetry are marked by  $\oplus$  and O(2) and O(10) are labeled.

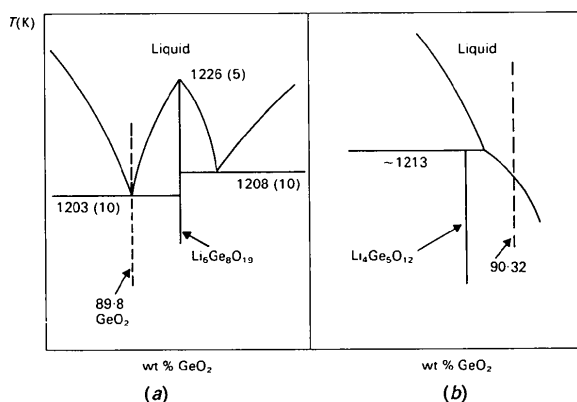


Fig. 4. (a) Portion of the phase diagram (Murthy & Ip, 1964) near 90 wt %  $\text{GeO}_2$  and 1213 K. (b) The type of peritectic transformation near 90 wt %  $\text{GeO}_2$  and 1213 K that is consistent with our data.

### $\text{Li}_2\text{O—GeO}_2$ phase diagram

Based on a number of crystal-growth experiments we see no evidence of the existence of the congruently melting phase ' $\text{Li}_6\text{Ge}_8\text{O}_{19}$ ' reported by Murthy & Ip (1964) and illustrated in Fig. 4(a). We have however grown large crystals of the compound  $\text{Li}_4\text{Ge}_5\text{O}_{12}$  under quasi-equilibrium conditions and believe it to be an equilibrium phase in the  $\text{Li}_2\text{O—GeO}_2$  system. In addition our data suggest that  $\text{Li}_4\text{Ge}_5\text{O}_{12}$  may form by a peritectic reaction of the type illustrated in Fig. 4(b). This is supported by the observation that  $\text{Li}_4\text{Ge}_5\text{O}_{12}$  crystals were grown from a melt of composition  $\text{Li}_6\text{Ge}_8\text{O}_{19}$  and the observation that crystals of  $\text{Li}_4\text{Ge}_5\text{O}_{12}$  could *not* be grown from a melt of composition  $\text{Li}_4\text{Ge}_5\text{O}_{12}$ . Furthermore, the reported eutectic temperatures in this region are uncertain to  $\pm 10$  K.

Differential thermal analysis (DTA) and room-temperature X-ray diffraction experiments were performed to determine which phases exist in equilibrium at temperatures and compositions close to those used during crystal growth. The DTA measurements were abandoned because our minimum heating and cooling rates were too rapid for equilibrium to be attained. In addition, considerable thermal hysteresis and the presence of metastable side reactions complicate the thermograms. Problems similar to these were reported by West & Blake (1976) for the  $\text{Li}_2\text{GeO}_3\text{—Na}_2\text{GeO}_3$  system. X-ray diffractograms of rapidly cooled samples indicated that they contained non-equilibrium phase mixtures typical of samples that are non-uniformly cooled. Additionally it should be noted that there is a strong tendency towards glass formation for compositions above 65 wt %  $\text{GeO}_2$  (Shelby & Ruller, 1987).

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### References

- DOUGHERTY, J. P. & KURTZ, S. K. (1976). *J. Appl. Cryst.* **9**, 145–158.
- IKEDA, T. & SATO, H. (1984). *Jpn. J. Appl. Phys.* **23**, 815–819.
- LOIACONO, G. M., SHONE, M. F., MIZELL, G., POWELL, R. C., QUARLES, G. T. & ELOUADI, B. (1986). *Appl. Phys. Lett.* **48**, 622–623.
- MURTHY, M. K. & IP, J. (1964). *J. Am. Ceram. Soc.* **47**, 328–331.
- SHELBY, J. E. & RULLER, J. (1987). *Phys. Chem. Glasses*, **28**, 262–268.
- SHELDRIK, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet R3m/V crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

VOLLENKLE, H. (1980). *Z. Kristallogr.* **153**, 131–139.

VOLLENKLE, H. & WITTMAN, A. (1968a). *Monatsh. Chem.* **99**, 244–250.

VOLLENKLE, H. & WITTMAN, A. (1968b). *Monatsh. Chem.* **99**, 251–254.

VOLLENKLE, H. & WITTMAN, A. (1969). *Z. Kristallogr.* **128**, 66–71.

VOLLENKLE, H. & WITTMAN, A. (1970). *Monatsh. Chem.* **101**, 46–56.

VOLLENKLE, H. & WITTMAN, A. (1971). *Monatsh. Chem.* **102**, 361–372.

WEST, A. R. & BLAKE, A. J. (1976). *J. Mater. Sci.* **11**, 801–808.

WITTMAN, A. & MODERN, E. (1965). *Monatsh. Chem.* **96**, 581–582.

*Acta Cryst.* (1990). **C46**, 2026–2028

## Crystal Chemistry of *cyclo*-Hexaphosphates. VIII. Structure of Hydroxylammonium *cyclo*-Hexaphosphate Tetrahydrate

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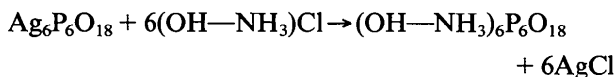
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**Abstract.**  $(\text{NH}_3\text{OH})_6\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$ ,  $M_r = 750.11$ , triclinic,  $P\bar{1}$ ,  $a = 10.365$  (5),  $b = 9.278$  (4),  $c = 7.280$  (3) Å,  $\alpha = 108.39$  (5),  $\beta = 100.30$  (5),  $\gamma = 96.02$  (5)°,  $V = 643.8$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.934$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 0.553$  mm<sup>-1</sup>,  $F(000) = 388$ ,  $T = 298$  K, final  $R = 0.028$  for 4750 reflections. The centrosymmetric  $\text{P}_6\text{O}_{18}$  ring anion is located at the centre of the unit cell. Three crystallographically independent hydroxylammonium groups co-exist in the atomic arrangement. The three-dimensional hydrogen-bond network is described.

**Introduction.** Investigation of organic cation-*cyclo*-hexaphosphates has been recently initiated by the characterization of the tris(ethylenediammonium) *cyclo*-hexaphosphate,  $(\text{NH}_3\text{—CH}_2\text{—CH}_2\text{—NH}_3)_3\text{—P}_6\text{O}_{18}\cdot 2\text{H}_2\text{O}$  (Durif & Averbuch-Pouchot, 1989). In the present work we describe the preparation and crystal structure of a second example for such compounds, the hydroxylammonium *cyclo*-hexaphosphate tetrahydrate,  $(\text{NH}_3\text{OH})_6\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$ .

**Experimental.** Crystals of the title compound have been prepared by using a metathesis reaction similar to that described by Boule (1938) for the preparation of water soluble *cyclo*-triphosphates. Here the starting material is  $\text{Ag}_6\text{P}_6\text{O}_{18}\cdot \text{H}_2\text{O}$  recently characterized by Averbuch-Pouchot (1989). Schematically the reaction is:



Crystals obtained by slow evaporation of an aqueous solution at room temperature have various morphologies: stout triclinic prisms or thick diamond-like plates. The title compound is stable at

room temperature. Crystal size:  $0.40 \times 0.40 \times 0.35$  mm. Density not measured. Philips PW1100 diffractometer, graphite monochromator. 19 reflections ( $12.0 < \theta < 18.0^\circ$ ) for refining unit-cell dimensions.  $\omega$  scan, scan width  $1.20^\circ$ , scan speed  $0.02^\circ \text{ s}^{-1}$ . Total background measuring time 6 s. 5532 reflections collected ( $3 < \theta < 35^\circ$ ),  $\pm h$ ,  $\pm k$ ,  $l$ ,  $h_{\text{max}} = 16$ ,  $k_{\text{max}} = 14$ ,  $l_{\text{max}} = 11$ .  $\text{Sin}\theta/\lambda = 0.81$  Å<sup>-1</sup>. Two orientation and intensity control reflections ( $\bar{7}01$  and  $70\bar{1}$ ) measured every four hours without any significant variation. 5169 reflections obtained after averaging Friedel pairs ( $R_{\text{int}} = 0.008$ ). Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN78*, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms located by difference Fourier syntheses. Anisotropic full-matrix least-squares refinement (on  $F$ ), isotropic for H atoms. Unit weights. Final refinements with 4750 reflections corresponding to  $I > 4\sigma_I$ . Final  $R = 0.028$  ( $wR = 0.033$ ),  $S = 0.438$ , max.  $\Delta/\sigma = 0.07$ , max. peak height in the final difference Fourier synthesis =  $0.425 \text{ e } \text{Å}^{-3}$ . Secondary extinction not refined. Scattering factors for neutral atoms and  $f'$ ,  $f''$  from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Enraf-Nonius (1977) *SDP* used for all calculations, on a MicroVAX II computer.

**Discussion.** Table 1 reports the final atomic coordinates.\*

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53118 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.