08.2–25   CRYSTAL STRUCTURE OF THE PHASE IV OF RbLiSO$_4$. By W.Steurer,H.Wittmann and H. Jagodzinski, Inst.f.Kristallographie und Mineralogie d.Universität, Theresienstr. 41, D-8000 München 2, FRG and A.Pietraszko, Inst. of Low Temperatures and Structure Research of the Polish Academy of Sciences, POB 937, 50-950, Wroclaw, Poland.

The structure of the commensurate modulated phase IV was determined by single crystal X-ray diffractometry at 446 K. Space group: P11n(No.7),Z=20,a=9.157(1),b=5.316(1),c= 43.654(3)Å,γ=89.97(1)$^\circ$,U=2125Å^3,D$_x$=2.95Mgm^{-3}, R=0.073,R$_w$=0.047 for 1862 reflexions (I>0).

The fivefold superstructure parallel c is caused by the ordering of the SO$_4$ tetrahedra. If we designate a right(left)-hand rotation around c by +(-) then the sequence of the SO$_4$ groups in one unit cell can be described by: ++-++--+-- (phase I:$\pm\pm$, phase III:--++, phase V$_{442K}$:+-, phase V$_{rt}$:-+ (A.Pietraszko and H. Jagodzinski(1984).Submitted to Z.Kristallogr.)). To facilitate the comparison of the different phases, refinements of the high temperature phase I and the average structures of the phases III and IV were performed using split positions or anharmonic temperature factors, and the probability density functions of all atoms were calculated (program Prometheus. U.H.Zucker,E.Perenthaler,W.F.Kuhs,R.Bachmann and H.Schulz(1983).J.Applied Cryst.16,358). The structural relationships between the different phases will be discussed.

8.824(2), b = 6.633(2), c = 13.977(4) Å, and Z = 4. The structure is characterized by infinite double chains $\frac{1}{\infty}$[Ge$_2^{II}$Ge$_2^{IV}$S$_8$]$^{4-}$ held together by Tl$^+$ cations. The double chains are composed of Ge-S single chains containing alternately divalent and tetravalent Ge atoms. These single chains are linked in pairs by S bridges between the Ge(II) and Ge(IV) atoms. As in typical thiogermanates(IV), the tetravalent Ge atoms are tetrahedrally coordinated to four S atoms (mean distance Ge(IV)-S: 2.224 Å). The divalent Ge atoms are bonded to three atoms forming with them ψ-tetrahedral arrangements (mean distance Ge(II)-S: 2.355 Å). The lone electron pair of the GeS$_3$E tetrahedron is directed towards a Tl atom at a distance of 3.106 Å only. The nine S atoms around Tl(2) form a distorted tricapped trigonal prism. With Tl(1), one of the S atoms is replaced by a Ge(II) atom (mean distance Tl-S: 3.437 Å).

Tl$_6$Ge$_2$Te$_6$ is triclinic, space group P$\overline{1}$, with a = 9.471(2), b = 9.714(2), c = 10.389(2) Å, α = 89.39(1), β = 97.27(1)$^\circ$, γ = 100.79(1)$^\circ$, and Z = 2. The structure is built from Ge$_2$Te$_6$ units with Ge-Ge bonds which are linked in a three-dimensional structure by Tl atoms coordinated to essentially six Te atoms. The Ge atoms are tetrahedrally bonded to three Te atoms and one further Ge atom. The most important mean distances are: d(Ge-Ge) = 2.456 Å, d(Ge-Te) = 2.573 Å, and d(Tl-Te) = 3.511 Å. The lone 6s electron pairs of Tl(I) display significant stereochemical activity.

08.2–26   STRUCTURAL CHEMISTRY OF TERNARY THALLIUM CHALCOGENIDES: THE CRYSTAL STRUCTURES OF Tl$_4$SiS$_4$, Tl$_4$SiSe$_4$, Tl$_2$Ge$_2$S$_4$, AND Tl$_6$Ge$_2$Te$_6$. G. Eulenberger, Institute of Chemistry, Hohenheim University, D-7000 Stuttgart 70, Federal Republic of Germany.

The title compounds were prepared from the elements by thermal synthesis. The determination of the crystal structures was based on single crystal intensity measurements carried out on a four-circle diffractometer (experimental absorption corrections by ψ scans).

Tl$_4$SiS$_4$ is monoclinic, space group Cc with a = 12.518(3), b = 11.241(2), c = 7.567(2) Å, β = 112.80(2)$^\circ$, and Z = 4. The structure is composed of tetrahedral [SiS$_4$]$^{4-}$ anions (mean distance Si-S: 2.130 Å) and Tl$^+$ cations, each surrounded by six S atoms. The compound is isostructural with Tl$_4$GeS$_4$ (G. Eulenberger, Z. Kristallogr. (1977), 145, 427). New structural aspects will be discussed.

Tl$_4$SiSe$_4$ crystallizes in the monoclinic system as well, space group C 2/c with a = 11.664(9), b = 7.277(4), c = 24.903(12) Å, β = 99.93(5)$^\circ$, and Z = 8. In analogy to Tl$_4$SiS$_4$, the structure is characterized by tetrahedral [SiSe$_4$]$^{4-}$ anions (mean distance Si-Se: 2.272 Å) connected by Tl$^+$ cations at five sets of positions. The SiSe$_4$ tetrahedra build up slabs composed of two layers of SiSe$_4$ tetrahedra parallel (001). The central plane between them is occupied by Tl atoms. These SiSe$_4$ double layers are again linked by the remaining Tl atoms arranged in parallel slabs. Each of three Tl atoms is coordinated to six Se atoms. The two further Tl atoms are in (5+1)- and 4-coordination, respectively, and exhibit strong stereochemical activity of the lone 6s electron pair of univalent thallium.

Tl$_2$Ge$_2$S$_4$ is orthorhombic, space group Pnma with a =

08.2–27   STRUCTURE AND BONDING IN URANIUM(IV) COM= PLEXES CONTAINING THE UO$_2$X$_4$ (X = Cl, Br) CHROMOPHORE

By J.F de Wet and M.R Caira, Crystallography Group, Chemistry Department, University of Port Elizabeth, Port Elizabeth, South Africa.

In octahedrally co-ordinated complexes of uranium containing the UO$_2$X$_4$ (X = Cl, Br) chromophore the bonding distances involving uranium have been observed to display a complementary axial-equatorial relationship (J.F. de Wet and J.G.H. du Preez, J.C.S. (Dalton), 1978, 592-596). Specifically, the shorter the (axial) U-O bonds, the longer the (equatorial) U-X bonds, which adopt a more-or-less square planar configuration, and vice versa. These effects may be interpreted in terms of the predominantly ionic character of uranium in such complexes, and of the resulting ligand-ligand repulsions; the effects are, however, small, and require accurate structure determinations.

We report here on the structural data obtained on six further U(IV) complexes of the type UX$_4$L$_2$ (Table 1), where L is an oxygen donor ligand terminating in R=O (R = C,S,P,As). The structure determinations were based on data in which errors due to absorption were eliminated as far as possible.

The U-X and U-O bond lengths observed in these structures confirm and extend the evidence found previously for axial-equatorial relationships (loc.cit.), with mean values (in Å) for U-X and U-O in each structure, respectively: 1: 2.605(3), 2.248(6); 2: 2.604(8), 2.249(12);   3: 2.607(8), 2.268(17); 4: 2.770(1), 2.218(8);   5: 2.619(3), 2.231(7); 6: 2.804(7), 2.145(34.

Ligand	Halogen	Crystal Data
1 $(Me_2CHCH_2)_2SO$	Cl	a=10.10, b=10.43, c=13.29Å; β=106.36°; Z=2; P=2_1/c
2 $(MePhN)_2CO$	Cl	a=14.01, b=19.33, c=14.44Å; β=119.28°; Z=4; P2_1/n
3* $(MePhN)_2CO$	Cl	a=15.87, b=13.21, c=15.76Å; Z=4; Pna2_1
4 $(MePhN)_2CO$	Br	a=14.39, b=19.85, c=24.71Å; Z=8; Fddd
5** $(C_4H_8N)_3PO$	Cl	a=17.03, b=11.71, c=18.21Å; β=109.2°; Z=4; C2/c
6 Ph_3AsO	Br	a=10.24, b=15.79, c=12.19Å; β=100.94°; Z=2; p2_1

*polymorph of 2

**pyrrolidyl

08.2–28   THE CRYSTAL STRUCTURE OF α-EUCRYPTITE, LiAlSiO$_4$. By K.-F. Hesse, Mineralogisches Institut, Universität Kiel, D-2300 Kiel, Germany.

According to Winkler (Acta Cryst. (1953) 6, 99) the low temperature polymorph of LiAlSiO$_4$, α-eucryptite, is isostructural with phenakite, Be$_2$SiO$_4$, and willemite, Zn$_2$SiO$_4$, and has an ordered Al,Si distribution. However, no structure determination has been published. Natural and synthetic crystals of α-eucryptite have now been used for structure refinement. Crystallographic data: trigonal R$\bar{3}$, a$_{hex}$ = 13.473(3)Å, c$_{hex}$ = 9.001(2)Å, Z = 18. With 1895 (1467) non-equivalent reflections the refinement converged at residuals of R = 0.080 (0.054) and R$_w$ = 0.040 (0.042) for the natural (synthetic) crystal. The results of these structure determinations are: the structures consist of [(Al,Si)O$_4$] tetrahedra with (Al,Si)-O mean distance 1.689Å (1.688Å) and [Li-O$_4$] tetrahedra with Li-O mean distance 1.981Å (1.984Å). The (Al,Si)-O distances suggest statistical Al,Si distribution or microtwinning in both natural and synthetic α-eucryptite. The Giebe-Scheibe test, high-resolution electron microscopy and diffraction strongly favour statistical Al,Si distribution.

08.2–29   Pb$_8$[O$_2$(SO$_4$)(Si$_4$O$_{13}$)], A NEW TETRASILICATE. By R. Fröhlich, Institut für Kristallographie, Universität, D-7500 Karlsruhe, Germany

In the system PbO-PbSO$_4$-PbSiO$_3$ several ternary phases exist; the compound 8PbO·SO$_3$·4SiO$_2$ melts congruently at 785°C and shows no phase transitions (Billhardt, thesis, Karlsruhe, 1968). Single crystals can be prepared by slow cooling from 800°C to 600°C and subsequent annealing at 600°C. Crystal data: monoclinic space group P2$_1$/n; a=914.0(3), b=1955.4(6), c=1131.3(4) pm, β=89.68(3)°; Z=4. The structure was solved by Patterson and Fourier methods. The present value of R=0.115 for 2456 observed reflections is poor due to a preliminary absorption correction for the irregular shape of the crystal investigated. Further refinement is in progress. The basic building blocks of the structure are two tetrahedral [Pb$_4$O]$^{6+}$-units, a sulphate group, and the tetrasilicate anion shown below.
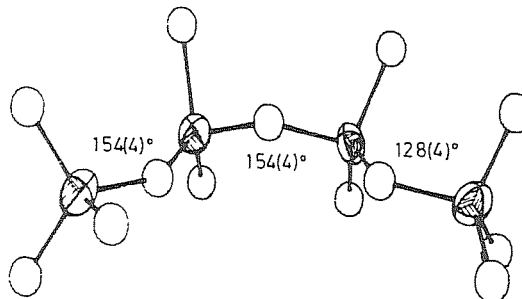
[Si$_4$O$_{13}$]$^{10-}$-ion; Si drawn as thermal ellipsoids.

08.2–30   THE CRYSTAL STRUCTURE OF Zn$_2$Ti$_{18}$S$_{32}$

By I. Kawada, M. Onoda and M. Saeki, National Institute for Research in Inorganic Materials, Sakura-mura, Ibaraki-ken 305, Japan.

Expecting tetrahedral coordination of metalsulfur in M-Ti-S system (M=metal), we have synthesized a new phase of Zn$_2$Ti$_{18}$S$_{32}$. (M. Saeki and M. Onoda, Chem. Lett. 1329, 1982). Obtained specimen was in powder form of dark gray color. 69 independent powder diffraction data were collected by an X-ray powder diffractometer using Cu- and Mo-target. Crystal system is cubic; a=9.843 Å. Taking no account of 2 very diffuse reflections, space group is Fd3m - O$_h^7$. Crystal structure was solved by crystal chemical considerations. The structure consists fundamentally of cubic closest packing of sulfur atoms. 16 Ti atoms occupy octahedral sites (Ti (1)) and 2 Ti atoms occupy statistically another 16 octahedral sites (Ti(2)). 2 Zn atoms occupy statistically 8 tetrahedral sites which are surrounded only by Ti(2) and S. (Table 1.). Considering very short distance between Zn and Ti(2) (2.13 Å), it is probable that Zn and Ti(2) do not simultaneously coexist at the nearest positions. If one takes account of the existence of diffuse reflections (e.g. 200 etc.), more detailed feature of the structure will be clarified.

Table 1.

		m	x	y	z	B
Zn	8(a)	1/4	1/8	1/8	1/8	2.39
Ti(1)	16(d)	1	1/2	1/2	1/2	1.35
Ti(2)	16(c)	1/8	0	0	0	0.02
S	32(e)	1	0.2504	0.2504	0.2504	0.92

number of reflections: 67, R=0.0695.