08.2–7 THE CRYSTAL STRUCTURES OF $NaKGeO_3$ AND K_2GeO_3. By E. Halwax and H. Völlenkle, Institut für Mineralogie, Kristallographie und Strukturchemie, TU Wien, A-1060 Wien, Austria.

The title compounds were synthesized by fusion of appropriate quantities of GeO_2, Na_2CO_3 and K_2CO_3 at 900 °C. Single crystals sealed in Lindemann-glass capillaries were investigated with a four-circle diffractometer (PW 1100) using MoKα radiation. The crystal structures of both compounds were solved by direct methods (MULTAN) and refined by the method of least squares.

Crystal data and parameters of refinement are: $NaKGeO_3$, $Pbn2_1$, Z=4, a=10.670(5), b=6.895(3), c=4.803(1) Å, D_x=3.434 gcm^{-3}, 527 independent observed reflections used for anisotropic refinement, R=0.048; K_2GeO_3, Pbca, Z=40, a=23.033(5), b=32.887(8), c=5.453(1) Å, D_x=3.197 gcm^{-3}, 2298 reflections used for isotropic refinement, R=0.123.

The crystal structures of both compounds contain infinite chains of composition $[GeO_3]_n^{-2n}$ extending parallel to the c axis (zweier single chains). The projection of the chains on (001) exhibits pseudohexagonal symmetry, very similar to Na_2GeO_3 (Cruickshank et al., Acta Cryst. B34 (1978) 1333). In Na_2GeO_3, however, this symmetry results from the nearly close-packed arrangement of the oxygen atoms, while this is no longer true for K_2GeO_3. In $NaKGeO_3$ ribbons of close-packed oxygen atoms have remained. The chains in the three structures differ essentially in symmetry ($mc2_1$ in Na_2GeO_3, 2_1 in $NaKGeO_3$, 1 and c for the three independent chains in K_2GeO_3).

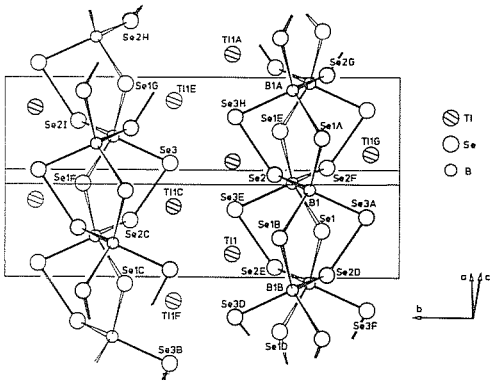
It is shown that a symmetry relation can be established between the structures of Na_2GeO_3, $NaKGeO_3$ and K_2GeO_3. The structure of K_2GeO_3 is in fact a 2x5x1 superstructure of a hypothetical structure whose space group Cmcm is a supergroup of the space groups of Na_2GeO_3 ($Cmc2_1$) and K_2GeO_3 (Pbca). The space group of $NaKGeO_3$ ($Pbn2_1$), on the other hand, is a minimal subgroup of the space group of Na_2GeO_3.

08.2–8 STRUCTURAL CHEMISTRY OF THALLIUM(I) THIOBORATES AND SELENOBORATES By B. Krebs and W. Hamann, Anorganisch-Chemisches Institut der Universität Münster, Corrensstr. 36, D-4400 Münster, Fed. Rep. of Germany

In binary and ternary boron sulfides so far known systems of corner-sharing trigonal planar BS_3 units are observed. $Na_3B_3S_6$, $K_3B_3S_6$ and the corresponding acid $H_3B_3S_6$ contain trimeric $B_3S_6^{3-}$ ions and $H_3B_3S_6$ molecules. In the unusual layer structure of B_2S_3 corner-sharing BS_3 groups form six-membered B_3S_3 and four-membered B_2S_2 rings. The novel porphin-like molecular B_8S_{16} and its polymeric chain isomer BS_2 contain as additional structural elements S_2 groups which connect the planar BS_3 units to form trithiadiborolane (-B-S-S-B-S-) rings. All these systems have significant B-S bonding (references: see B. Krebs, Angew. Chem. (1983) 95, 113; Angew. Chem. Int. Ed. (1983) 22, 113).

In the crystal structures of $TlBS_2$, $TlBS_3$, $TlBSe_3$, Tl_3BS_3 and Tl_3BSe_3, we could now show that the first three phases contain boron tetrahedrally coordinated by sulfur or selenium. Besides $Pb_4B_4S_{10}$ and $Ag_6B_{10}S_{18}$ they are the first examples for this high coordination number. $TlBS_2$ shows polymeric $(BS_2^-)_n$ ions built of alternating chair-like B_3S_3 rings and B_2S_2 rings linked at the tetrahedral boron sites. $TlBS_3$ and $TlBSe_3$ are the first "perthio-(seleno)borate" structures and contain non-planar trithiadiborolane rings which are spirocyclically linked by boron to form $(BS_3^-)_n$ and $(BSe_3^-)_n$ chains (Fig.).

In the ortho compounds Tl_3BS_3 and Tl_3BSe_3, on the other hand, trigonal planar BX_3 groups are observed which can be regarded as a new type of discrete BX_3^{3-} anions (X = S, Se). The crystal structure type appears to be yet unknown.



$TlBSe_3$

In the tetrahedral groups the mean B-S (B-Se) distances are 1.93 Å (2.06 Å), the mean trigonal B-S (B-Se) bond lengths are observed to be 1.83 Å (1.95 Å). Tl(I) is in irregular 8-, 9- and 10-coordination.

Crystal data: Tl_3BS_3: space group $P2_1/m$, a = 5.444(2), b = 9.699(3), c = 6.690(2) Å, β = 98.13(2)°, Z = 2, d_x = 6.84 $g \cdot cm^{-3}$; $TlBSe_3$: space group Cc, a = 7.256(2), b = 12.137(3), c = 7.051(2) Å, β = 128.93(3)°, Z = 4; d_x = 6.21 $g \cdot cm^{-3}$; Tl_3BSe_3: space group $P2_1/m$, a = 5.547(2), b = 10.099(3), c = 6.852(2) Å, β = 97.59(3)°, Z = 2, d_x = 7.51 $g \cdot cm^{-3}$ (see also B. Krebs, W. Hamann, Z. Kristallogr. (1983) 162, 149).