

PS-08.01.15 CRYSTAL STRUCTURE OF DIPOTASSIUMPENT-ABARIUMSILICATE,  $K_2Ba_5Si_{12}O_{30}$ . By R.P. Gunawardane\*, Dept. of Chemistry, University of Peradeniya, Sri Lanka & R.A.Howie, Dept. of Chemistry, University of Aberdeen, U.K.

Single crystals were grown from a melt of composition  $K_2O=8.3$ ,  $BaO=25.0$ ,  $SiO_2=66.7$  % mole. Crystal data:  $K_2Ba_5Si_{12}O_{30}$ , monoclinic,  $P2_1/m$ ,  $a=13.304(9)$ ,  $b=7.313(2)$ ,  $c=8.259(2)$  Å,  $\beta=100.02(1)$ ,  $Z=1$ ,  $D_m=3.29(3)$ ,  $D_x=3.32$  Mg  $m^{-3}$ . The structure was determined using 736 unique observed reflections measured on a Nicolet P3 four-circle diffractometer with Mo  $K\alpha$  radiation. The atomic coordinates were refined to  $R=0.063$ . The structure consists of infinite  $Si_2O_5$  sheets parallel to (100) linked through 8-coordinate K and 6-coordinate Ba atoms. A novel feature is the occurrence of unequal number of linked 4-, 6- and 8-membered rings of  $SiO_4$  in the sheets. The silicate tetrahedra are somewhat distorted and similarly, K and Ba cations occupy irregular polyhedra. The structure of  $K_2Ba_5Si_{12}O_{30}$  is closely related to those of  $K_2Ba_7Si_{14}O_{40}$  (Cervantes-Lee, F.J. et al. Acta Cryst. 1982, B38, 2099-2102) and high and low forms of  $BaSi_2O_5$ . The sheets in low  $BaSi_2O_5$  are more corrugated than in the high polymorph. Silicate layers in  $K_2Ba_7Si_{14}O_{40}$  are less folded than in  $BaSi_2O_5$ . It is apparent that the folding of silicate layers in the present structure ( $K_2Ba_5Si_{12}O_{30}$ ) is even less than in  $K_2Ba_7Si_{14}O_{40}$ .

PS-08.01.16 SYMMETRY OF NATURAL ILVAITE AND CRYSTAL STRUCTURE OF DEHYDROGENATED ILVAITE. By Y. Takéuchi\* and H. Sawada, Department of Earth Sciences, Nihon University, Tokyo, Japan.

The existence of polysynthetic twinings in the crystals of natural ilvaite  $Ca(Fe^{2+}Fe^{3+})Fe^{2+}[Si_2O_7]O_8H$  has been experimentally established by studying the profiles of high-order reflections such as 24,0,0 and 008 reflections; the former was step-scanned along  $c^*$  and the latter along  $a^*$  on an AFC-5S four-circle diffractometer, using graphite-monochromatized Mo $K\alpha$  radiation. The scanning was executed with an interval of 0.003 of the unit length of each reciprocal lattice row. The results show that in the case of crystals of high monoclinicity ( $\beta = 90.2^\circ \sim 90.3^\circ$ ) each reflection is in general split into a double peak, showing the coexistence of twinings on (001) and on (100) in the crystals. In the particular case of crystals with  $\beta = 90.0^\circ$ , each reflection tends to be broad and have shoulders. A profile-fitting procedure has suggested that those crystals consist of complex composite twins of monoclinic components with composition planes (001) and (100). Such a situation is similar to the cases of Mn-rich natural ilvaites which tend to have  $\beta = 90.0^\circ$  (Y. Takéuchi et al. Proc. Inst. Natural Sciences, Nihon Univ. 28, 1993, in press). Thus the existence of orthorhombic ilvaite in nature is unlikely.

Fig. 1 (i) shows an example of the intensity profile of the 008 reflection of a spherical crystal with diameter 0.21 mm obtained from a Kamioka ilvaite,  $a = 13.005(6)$  Å,  $b = 8.810(5)$  Å,  $c = 5.860(2)$  Å,  $\beta = 90.32(3)^\circ$ . By heating the same crystal in air at 950 K for 30 h and successively at 1020 K for 45 h, we obtained an orthorhombic phase which was free from twinings:  $a = 13.060(4)$  Å,  $b = 8.843(2)$  Å,  $c = 5.835(1)$  Å,  $Pnam$ . The shortened  $c$  length compares well with 5.830(2) Å for a

dehydrogenated ilvaite obtained by Robie et al. (Phys Chem Minerals, 15, 390-397, 1988) by heating powder samples to 913 K in vacuum. Although reflections from the crystal thus obtained are diffuse and weak [e.g. 008 reflection in Fig. 1 (ii)], an attempt has been made of studying its structure based on a set of 585 graphite-monochromatized Mo $K\alpha$  diffraction intensities,  $>3\sigma$  (I), collected on AFC-5S with the  $\omega$  scan mode. An isotropic refinement ( $R = 0.10$ ,  $wR = 0.11$  at the present stage), has brought out a marked shortening of the bond between the dehydrogenated oxygen atom, O(7), and Fe(1), the value being 1.819(15) Å which is smaller by about 8.5 % than the mean length of the O(7)-Fe(11) and O(7)-Fe(12) bonds in natural ilvaite.

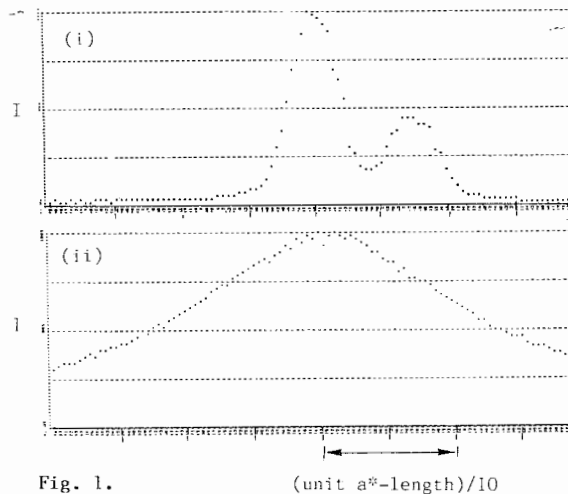


Fig. 1. (unit  $a^*$ -length)/10

PS-08.01.17 STRUCTURAL CHEMISTRY OF  $BaAl_4/ThCr_2Si_2$  TYPE COMPOUNDS. By G. Just and P. Paufler, Institute of Crystallography and Solid State Physics, University of Technology, Dresden, Federal Republic of Germany.

Lattice ratios  $c/a$  and structural parameters  $x_3$  of about 180 representatives of the  $BaAl_4$  type of structure (space group  $I 4/mmm$ ) have been critically reviewed taking binary and multicomponent phases into account. Leaving out data of minor reliability a considerable scatter of experimental values in a  $x_3$ - $c/a$  plane remains, which is classified according to the concepts of equal interatomic spacing and coordination polyhedra. Lines of equal spacing  $d$  were calculated for all positions in the unit cell up to  $d \leq 1.9$  a (a lattice parameter). Moreover, the coordination of all atom positions is given up to that distance. Several points in the  $x_3$ - $c/a$  plane were found to represent special structural features as, e.g., coordination polyhedra with coordination numbers 16, 18 or 20 for the barium position. Packing of distorted tetrahedra appears to determine those special states. Individual space requirements of atoms are met with different spacing conditions between Al(1) and Al(2) positions. Subdivision of representatives into families behaving similarly from the point of view of crystal chemistry is discussed.