08.2–19 CRYSTAL CHEMISTRY AND FERROELECTRIC PROPERTIES OF MIXED LAYERED COMPOUNDS IN THE SYSTEM Bi_2WO_6 - $Bi_4Ti_3O_{12}$. By V. K. Yanovsky and V. I. Voronkova, Moscow State University, Moscow 117234, USSR

This paper deals with the mixed layered compounds in the system Bi_2WO_6 - $Bi_4Ti_3O_{12}$. They are $Bi_6Ti_3WO_{18}$, $Bi_{10}Ti_3W_3O_{30}$, and a large number of similar crystalline phases found in the Bi_2WO_6 - rich region of the system. The structures of the above compounds are closely related to those of well-known layered crystals $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})$ but are built up as the ordered alternating stackings of perovskite-like fragments of various thickness and Bi_2O_2-sheets. So they may be represented by the general formula $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})(Bi_2O_2)(A_{p-1}B_pO_{3p+1})$...where A = Bi, and B is Ti, W, or a mixture of the latter.

There is the simple correlation between the composition and structure of these crystalline phases. In particular, the value of c-parameter is $c = N \cdot 4.13$ Å where N is the number of "elementary layers" (Bi_2O_2-sheets or one-octahedron layers in perovskite-like fragments), and 4.13 ± 0.03 Å is the average thickness of these layers. In turn, N is equal to the content of Bi atoms in the unit cell. For the studied compounds N can change from 4 to 44 (c ranges from 16.4 to about 183 Å).

Single crystals of $Bi_6Ti_3WO_{18}$ and $Bi_{10}Ti_3W_3O_{30}$ are grown from fluxed melts, and their physical properties are studied. At low temperatures the two compounds are polar, exhibit the orthorhombic lattice strains, and undergo the ferroelectric phase transitions at 750 and 735°C, respectively.

Similar mixed layered compounds are expected to exist in many other systems. Several of them have been synthesized by Kikuchi, et al.[1]

A great variety of such obtained and possible structures may be described by means of numerical symbols, nearly in the same manner as in the case of polytypic compounds.

1. T. Kikuchi, A. Watanabe, and K. Uchida. Mater. Res. Bull., 12, 299, 1977.

08.2–20 NEUTRON DIFFRACTION INVESTIGATION OF $K_2Se_2O_5$, $KHSeO_3$ AND $NaH(D)SeO_3$ SINGLE CRYSTALS. By N.N. Bydanov, I.S. Vinogradova, E.E. Rider and V.A. Sarin, Branch of Karpov Physico-Chemical Institute, Obninsk, USSR.

As a result of neutron diffraction study of $KHSeO_3$, $NaH(D)SeO_3$ and $K_2Se_2O_5$ single crystals using four-circle "Syntex" automatic neutron diffractometer the symmetry, the space groups and the unit cell parameters have been determined. The sets of room temperature integrated intensities have been obtained using $\lambda = 1.167$ Å, θ-2θ scan within the range $0 < \sin\theta/\lambda \leq 0.8$ Å^{-1}. The crystal structures of $K_2Se_2O_5$ and $KHSeO_3$ have been solved by the direct method. For $NaH(D)SeO_3$ the positions of H(D) have been found. The results are presented in Table.

	$K_2Se_2O_5$	$KHSeO_3$	$NaHSeO_3$ / $NaDSeO_3$
Space Group	Pbca	P$\bar{1}$	B2/b
a, Å	9.701(4)	5.003(6)	21.96(9) 21.94(14)
b	25.042(10)	5.726(10)	10.28(4) 10.29(6)
c	10.645(3)	6.729(3)	5.788(6) 5.782(9)
α, °	90	109.0(1)	90
β	90	107.3(1)	90
γ	90	91.3(1)	105.1(3) 105.2(4)
Z	16	2	16
ρ(calc.)	3.27	3.24	3.20-3.22
N(refl.)I	2656	1414	1732-1139
R	0.026	0.022	0.036-0.049
Se=O, Å	1.64-1.66	1.65-1.67	1.65-1.69 1.65-1.68
Se-O	1.83-1.86	1.78	1.72-1.77 1.71-1.76
O-H	-	0.99	0.98-1.03 1.00-1.01

The cations of potassium and sodium are surrounded by oxygen atoms of SeO_3 groups which compose the coordination sphere. $K_2Se_2O_5$ crystal is constructed of the layers of diselenite ions $Se_2O_5^{2-}$, which interchange with potassium layers. Diselenite ion consists of two SeO_3 groups, which have common oxygen atom. The disordering of no element of structure is found. In $KHSeO_3$ crystal $HSeO_3^-$ ions are connected in dimers by hydrogen bond O-H...O(O...O 2.75 Å, O-H...O 165.3°). The disordering of H is not observed. In $NaHSeO_3$ and $NaDSeO_3$ $H(D)SeO_3^-$ ions are also connected in dimers, but of two types. And the disordering of H(D) is found in one type of dimers. Hydrogen bonds are 2.60...2.68 Å, with the angles of 168 - 173°.