## **PS08.01.29 ISOMORPHOUS REPLACEMENTS IN FLUO-RITES AND SILLENITES** V.I.Simonov, Institute of Crystallography, Moscow 117333, Russia

On the basis of the data obtained from accurate X-ray and neutron diffraction structure studies we analyzed the character of isomorphous replacements in fluorite-related single crystals in the MF2-R2F3 system, where M=Ca, Sr, Ba; R=Y, La, Pr, Lu and sillenites Bi12M1±xO20±y, where M=Ge, Ti, (Fe, P), (Bi, Ga), (Bi, Fe), (Bi, Zn), (Bi, V). In single crystals of solid solutions with the fluorite-related structure the known clusters Ln<sub>4</sub>F<sub>26</sub> or Ln<sub>6</sub>F<sub>36</sub> are formed, depending on the relation of ionic radii of M2+ and R3+ cations. If a large number of M2+ cations are replaced by R3+ cations, more complex clusters are formed with a simultaneous probable accommodation of complementary F1- anions on the two and threefold symmetry axes. The mechanism of isomorphous replacements in sillenite structures is totally different. In contrast to the fact that the valence of a M cation is always +4, while the number of oxygen atoms is strictly 20, as was always reported in the literature, in the above compounds the effective valences of M cations are different. For instance, in (Bi,Zn)-sillenite it is less than +4, a Ge-sillenite it equals +4, while in (Bi,V) it exceeds +4. The amount of oxygen is also different. When Bi cations in the isomorphic mixture with other cations occupy the M site in the structure, their valence in all the cases was found Bi3+. In fact, in this case MO4 tetrahedron are replaced by umbrella-like BiO3 groups, the statistics of these groups being in accordance with their orientation. The average cubic symmetry is retained over the entire crystal structure. The site of the fourth missing oxygen atom in the BiO3 group is occupied by electron lone pair of a Bi atom. Pentavalent V5+ at the M site results in the occupation of structure voids by additional O atoms. The lability of sillenite framework is so great that Fe2+ and P5+ cations with totally different ionic radii are allowed to occupy statistically the M site. The unusually remarkable isomorphism of cations in fluorites and sillenites permits controlled changes of physical properties of these compounds.

**PS08.01.30 STRUCTURAL RELATIONSHIPS AMONG Cs<sub>3</sub>MI<sub>5</sub> PHASES.** Rune Sjövall and Christer Svensson, Dept. of Inorganic Chemistry 2, Lund University, P.O. Box 124, S-221 00 Lund, Sweden.

Compounds  $C_{s_3}MI_5$  with M a *d*-element crystallize in a limited number of type structures. We have investigated structures with separate  $MI_{4^2}$ - ions and infinite nets of composition ( $Cs_3I$ )<sup>2+</sup>.

The main structure types are those of Cs<sub>3</sub>CoCl<sub>5</sub> [1] represented by Cs<sub>3</sub>MnI<sub>5</sub>, space group *I* 4/*mcm* with a = 10.187(1), c = 16.574(1) Å, and (NH<sub>4</sub>)<sub>3</sub>ZnCl<sub>5</sub> [2] represented by Cs<sub>3</sub>CdI<sub>5</sub>, space group *Pnma* with a = 10.036(1), b = 11.852(1), c = 14.850(1) Å.

There is also the Cs<sub>3</sub>HgI<sub>5</sub> type [3] in space group *Pbca* with a = 18.789(3), b = 18.433(3), c = 10.106(2) [4]. A mixed Cd-Hg compound with composition Cs<sub>3</sub>(Cd<sub>0.52</sub>Hg<sub>0.48</sub>)I<sub>5</sub> crystallize in the same type with a = 18.771(2), b = 18.439(3), c = 10.118(2) Å. Further, we have found a new superstructure for another form of Cs<sub>3</sub>CdI<sub>5</sub>with space group *Pbca* and a = 18.893(1), b = 37.015(4), c = 10.085(1) Å.

The  $Cs_3MnI_5$  structure is a distorted antitype of perovskite with corner shared octahedra of Cs<sup>+</sup> around central I<sup>-</sup> ions, and MI<sub>4</sub><sup>2-</sup> ions corresponding to the large cations of perovskite. The other structures in space groups *Pnma* and *Pbca* are antitypes of BaNiO<sub>3</sub> with different orientations of the tetrahedral ions corresponding to the Ba<sup>2+</sup> ions and slightly different displacements of the infinite chains of Cs<sup>+</sup> octahedra (around I- ions) sharing opposite faces.

## References:

[1] H.M. Powell and A.F. Wells (1935) J. Chem. Soc. 1935, 359-362.

[2] H.P. Klug and L. Alexander (1944) J. Amer. Chem. Soc. 66, 1056-1064.

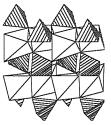
[3] P.M. Fedorov, V.I. Pakhomov and I.N.Ivanova-Korfini (1975) *Koordin. Khim.* 1, 1569-1571.

[4] R. Sjövall and C. Svensson (1988) Acta Crystallogr. C44, 207-210.

PS08.01.31 [4+2]-COORDINATED MOLYBDENUM IN THE CHAIN STRUCTURE OF Rb<sub>2</sub>Cu<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>. S.F.Solodovnikov, Z.A.Solodovnikova, V.I.Alekseev, Institute of Inorganic Chemistry, Novosibirsk, Russia

The atomic arrangement of  $Rb_2Cu_2(MoO_4)_3$  with a new structure type was determined. The main features of the structure are the following: (i) couples of infinite wolframite-like ribbons of  $CuO_{(4+2)}$ -octahedra running along [010] and sharing vertices with two topologically different types of bridging MoO<sub>4</sub>-tetrahedra (fig.), (ii) the tetradentate MoO<sub>4</sub>-tetrahedra sandwiched between two such ribbons interact weakly with each other to give CN = 4 + 2 for molybdenum, (iii) the separate couples of the ribbons are connected in the structure by rubidium atoms.

The new structure type represented by  $A_2Cu_2(MoO_4)_3$  (A = Rb, Cs) only completes the morphotropic series of double molybdates  $A_2M_2(MoO_4)_3$  (A = K, Rb, Cs, Tl; M = Mg, Mn, Co, Ni, Cu, Zn, Cd) which were known to possess the structures of  $K_2Zn_2(MoO_4)_3$ ,  $K_2Mn_2(MoO_4)_3$  or  $K_2Mg_2(SO_4)_3$  (langbeinite). The substantial difference of the  $Rb_2Cu_2(MoO_4)_3$  type with a chain structure from the other structures containing frameworks of



 $M^{2+}O_{6}$ -octahedra and  $MoO_{4}$ -tetrahedra seems to be caused by stereochemical peculiarities of Cu(II).

Synthesis: the light green needle-like crystals were obtained by spontaneous crystallization of the mixture  $CuMoO_4 + Rb_2Mo_2O_7$  from 650 to 400°C at cooling rate of 3°/hr.

Crystal data: monoclinic, sp. gr. C2/c, a = 27.698(2), b = 5.102(1), c = 19.292(1) Å,  $\beta = 107.26(1)^{\circ}$ , Z = 8,  $\lambda$ MoK $\alpha$ , R = 0.016 for 882 I > 3 $\sigma$ (I).

Interatomic distances: Mo-O (tetrahedra) 1.708-1.814 Å, Mo-O ([4+2]-coordination) 1.708-1.859 + 2.545 + 2.853 Å, Cu-O ([4+2]-coordination) 1.914-2.743 Å, Rb-O 2.816-3.924 Å (CN = 9-10).

## PS08.01.32 PSEUDO-SYMMETRY IN STRUCTURE OF Re<sub>6</sub>Se<sub>7</sub>Br<sub>4</sub>. N. L. Speziali and C. B. Pinheiro, Departamento de Física, ICEx - UFMG, Belo Horizonte - Brazil

A number of compounds presenting rhenium octahedral clusters in their structures have been investigated and related to Chevrel phase in molybdenum compounds. The ternary compounds  $\operatorname{Re}_{6}X_{i}Y_{j}$  (Y=Cl, Br and X=Se,S) crystallize with well defined clusters of  $\operatorname{Re}_{6}L_{8}$  (L=X and/or Y), where the Re atoms define an octahedron and are placed in the center of a cube defined by the 8 L atoms. The L atoms are called inner ligands. The link between the clusters is made, in general, via Y elements.

The crystal structure of many compounds in  $\text{Re}_6X_iY_j$  family have been investigated for different type and number of inter-cluster atoms. The 12 d<sup>4</sup> state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f<sup>14</sup>5d<sup>5</sup>6s<sup>2</sup> state). The 18 remainder electrons are used in a subtle charge transfer through ionic bonds with halogen and chalcogen atoms. It has been reported that controlling the chalcogen number i and the halogen number j, preserving the number of valence electrons i+2j=18, structures with Re<sub>6</sub>L<sub>8</sub> clusters linked by halogen bridges in one, two or three directions of the space can be obtained.

Structure of  $\text{Re}_6\text{Se}_7\text{Br}_4$  single crystal has been studied. In this crystal,  $\text{Re}_6\text{ISe}_7\text{Br}$  clusters link each other via halogen bridges in a three dimensional way. It was evidenced that a monoclinic C12/ c1 symmetry is more suitable to describe the structure than the rombohedric  $\overline{\text{R3}}$  c assumed by other authors. The real monoclinic structure has in fact a pseudo-rhombohedral symmetry: the position of the linking Br atoms can not be described by the  $\overline{\text{R3}}$  c space group.