

**PS08.01.29 ISOMORPHOUS REPLACEMENTS IN FLUORITES 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  $MF_2-R_2F_3$  system, where  $M=Ca, Sr, Ba$ ;  $R=Y, La, Pr, Lu$  and sillenites  $Bi_{12}M_{1\pm}O_{20\pm}$ , 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  $Ln_4F_{26}$  or  $Ln_6F_{36}$  are formed, depending on the relation of ionic radii of  $M^{2+}$  and  $R^{3+}$  cations. If a large number of  $M^{2+}$  cations are replaced by  $R^{3+}$  cations, more complex clusters are formed with a simultaneous probable accommodation of complementary  $F^-$  anions on the two and three-fold 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 isomorphous mixture with other cations occupy the M site in the structure, their valence in all the cases was found  $Bi^{3+}$ . In fact, in this case  $MO_4$  tetrahedra are replaced by umbrella-like  $BiO_3$  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  $BiO_3$  group is occupied by electron lone pair of a Bi atom. Pentavalent  $V^{5+}$  at the M site results in the occupation of structure voids by additional O atoms. The lability of sillenite framework is so great that  $Fe^{2+}$  and  $P^{5+}$  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  $Cs_3MI_5$  PHASES.** Rune Sjövall and Christer Svensson, Dept. of Inorganic Chemistry 2, Lund University, P.O. Box 124, S-221 00 Lund, Sweden.

Compounds  $Cs_3MI_5$  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  $(Cs_3I)^{2+}$ .

The main structure types are those of  $Cs_3CoCl_5$  [1] represented by  $Cs_3MnI_5$ , space group  $I4/mcm$  with  $a = 10.187(1)$ ,  $c = 16.574(1)$  Å, and  $(NH_4)_3ZnCl_5$  [2] represented by  $Cs_3CdI_5$ , space group  $Pnma$  with  $a = 10.036(1)$ ,  $b = 11.852(1)$ ,  $c = 14.850(1)$  Å.

There is also the  $Cs_3HgI_5$  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  $Cs_3(Cd_{0.52}Hg_{0.48})I_5$  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  $Cs_3CdI_5$  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  $Cs^+$  around central  $I^-$  ions, and  $MI_4^{2-}$  ions corresponding to the large cations of perovskite. The other structures in space groups  $Pnma$  and  $Pbca$  are antitypes of  $BaNiO_3$  with different orientations of the tetrahedral ions corresponding to the  $Ba^{2+}$  ions and slightly different displacements of the infinite chains of  $Cs^+$  octahedra (around  $I^-$  ions) sharing opposite faces.

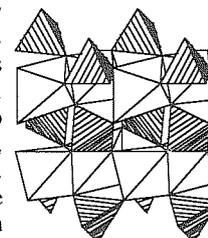
**References:**

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**PS08.01.31 [4+2]-COORDINATED MOLYBDENUM IN THE CHAIN STRUCTURE OF  $Rb_2Cu_2(MoO_4)_3$ .** 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  $MoO_4$ -tetrahedra (fig.), (ii) the tetradentate  $MoO_4$ -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 30/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  $Re_6Se_7Br_4$ .** 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  $Re_6X_iY_j$  ( $Y=Cl, Br$  and  $X=Se, S$ ) crystallize with well defined clusters of  $Re_6L_8$  ( $L=X$  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  $Re_6X_iY_j$  family have been investigated for different type and number of inter-cluster atoms. The 12  $d^4$  state single-covalent-Re-Re bonds involves 24 of 42 valence electrons (6 Re atoms in  $4f^{14}5d^56s^2$  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  $Re_6L_8$  clusters linked by halogen bridges in one, two or three directions of the space can be obtained.

Structure of  $Re_6Se_7Br_4$  single crystal has been studied. In this crystal,  $Re_6L_8$  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 rhombohedral  $R\bar{3}c$  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  $R\bar{3}c$  space group.