PS08.01.29 ISOMORPHIC 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 fluoride-related single crystals in the $M_2F_3$ system, where $M$ = Cs, Sr, Ba; $R=F$, $Cl$, $Br$, $I$ and silenite $Bi_2Mn_5O_{15}$, where $M$ = Ge, Ti, (Fe, P), (Bi, Ga), (Bi, Fe), (Bi, Zn), (Bi, V). In single crystals of solid solutions with the fluoride-related structure the known clusters $Li_F$ or $La_F$ are formed, depending on the relation of ionic radii of $M^+$ and $R^+$ cations. If a large number of $M^+$ cations are replaced by $R^+$ cations, more complex clusters are formed with a simultaneous probable accommodation of complementary $F^-$ or $I^-$ on the two and threefold symmetry axes. The mechanism of isomorphous replacements in silenites 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,Fe) and (Bi,Zn) infinite nets of composition $Cs_9Bi_{15}O_{28}$ are formed. While in Bi-based cations 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 $MoO_4$ tetrahedra are replaced by umbrella-like $BiO_5$ 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 $BiO_5$ group is occupied by electron lone pair of a Bi atom. Pentavalent V$^{5+}$ at the site results in the occupation of structure voids by additional O atoms. The lability of silenite framework is so great that $FeO_4$ and $PbO_4$ $M^+$ cations with totally different ionic radii are allowed to occupy statistically the $M$ site. The unusually isomorphous isomorphism of cations in fluorites and silenites permits controlled changes of physical properties of these compounds.

PS08.01.30 STRUCTURAL RELATIONSHIPS AMONG CS$_3$M$_2$ PHASES. Rune Sjövall and Christer Svensson, Dept. of Inorganic Chemistry, Lund University, PO. Box 124, S-221 00 Lund, Sweden

Compounds $Cs_3M_2$ with $M$ a $d$-element crystallize in a limited number of type structures. We have investigated structures with separate $M_2$-ions and $Cs_3$-ions in their structures.

The main structure types are those of $Cs_3CoCl_5$ [1] represented by $Cs_3MnF_5$, space group $I4_{1}mcm$ with $a = 10.187(1)$, $c = 16.574(7)$ Å, and ($NH_4$)$_2$ZnCl$_5$ [2] represented by $Cs_3CdCl_5$, space group $Pmna$ with $a = 10.085(1)$, $b = 11.852(4)$, $c = 14.850(1)$ Å.

There is also the $Cs_3HfCl_5$ type [3] in space group $Pmca$ with $a = 18.789(3)$, $b = 18.433(2)$, $c = 10.105(2)$. A mixed $Cs_3HfF_5$ compound with composition $Cs_3(CdF_5)(HfF_5)$ crystallizes in the same type with $a = 18.771(2)$, $b = 18.498(3)$, $c = 10.118(2)$ Å. Further, we have found a new superstructure for another form of $Cs_3CdF_5$ with space group $Pmca$ and $a = 18.805(3)$, $b = 27.015(4)$, $c = 10.055(1)$ Å.

The $Cs_3M_2$ structure is a distorted antitype of perovskite with corner shared octahedra of $Cs^+$ around central $I^-$, and $M_2^2$-ions corresponding to the large cations of perovskite. The structures in space groups $Pmca$ and $Pmna$ are analogues of Ba$_2$O$_4$ with different orientations of the tetrahedral ions corresponding to the Ba$^{2+}$ ions and slightly distorted octahedrons of the infinite chains of $Cs^+$ octahedra around $I^-$ ions sharing opposite faces.

References:

PS08.01.31 [4+2]-COORDINATED MOLYBDENUM IN THE CHAIN STRUCTURE OF $Rb_2Cu_2(MoO_4)_2$. S.P. Solodovnikov, Z.A. Solodovnikova, V.I. Aleksseev, Institute of Inorganic Chemistry, Novosibirsk, Russia

The atomic arrangement of $Rb_2Cu_2(MoO_4)_2$ with a new structure type was determined. The main features of the structure are the following: (i) couples of infinite wolframite-like ribbons of $CuO_4$-$MoO_4$-octahedra running along $[010]$ and sharing vertices with two topologically different types of bridging $MoO_4$-tetrathedra (fig.), (ii) the tetradenate $MoO_4$-tetrathedra 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 via nickelidum chains. The new structure type represented by $A_2Cu_2(MoO_4)_2$ ($A = Rb$, Cs) only completes the morphotropic series of double molybdates $A_2M_2(MoO_4)_2$ ($A = K$, $Rb$, Cs; $M = Mg$, Mn, Co, Ni, Cu, Zn, Cd) which were known to possess the structures of $K_2Zn_2(MoO_4)_2$, $K_2Mn_2(MoO_4)_2$, or $K_2Mg_2(SO_4)_2$ (langbeinite). The substantial difference between the $Rb_2Cu_2(MoO_4)_2$ type with a chain structure from the other structures containing frameworks of $MoO_4$-octahedra and $MoO_4$-tetrathedra 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 $CuMoO_4$ + $Rb_2MoO_4$ from 650 to 400°C at cooling rate of 5-20°C.

Crystal data: monoclinic, sp. gr. $C2/c$, $a = 27.698(2)$, $b = 5.102(1)$, $c = 19.292(1)$ Å. $\beta = 107.26(1)^0$. $Z = 8$, $\lambda MoK\alpha$, $R = 0.016$ for 8821 > 3$\sigma$(I).

Interatomic distances: $Mo-O$ (tetrathedra) 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 $Re_2Se_2Br_4$. N. L. Speziali and C. B. Pinheiro, Departamento de Física, ICEX - UFMG, Belo Horizonte - Brazil

A number of compounds presenting rhombohedral octahedral clusters in their structures have been investigated and related to Chevrel-phase in molybdenum compounds. The ternary compounds $Re_2X_2Y_4$ (X=Cl, Br and X=Se, S) crystallize with well defined clusters of $ReL_6$ (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 $Re_2X_2Y_4$ family have been investigated for different type and number of inter-cluster atoms. The 12 $d^8$ state single-element-Re-Re bonds involves 24 valence electrons (6 Re atoms in $4f^5$-6d$^6$ 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 $ReL_4$ clusters linked by halogen bridges in one, two or three directions of the space can be obtained.

The structure of $Re_2Se_2Br_4$ single crystal has been studied. In this crystal, $Re_2Se_2Br_4$ clusters link each other via halogen bridges in a three dimensional way. It was evidenced that a monoclinic $C2/c$ symmetry is more suitable to describe the structure than the rhombohedral $R3c$ 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 $R3c$ space group.