INORGANIC AND MINERAL COMPOUNDS

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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 fluoride-related single crystals in the [MgF2-RF2] system, where M=Ca, Sr; R=Y, La, Pr; Lu and silenites Bi2M2MoO19, where M=Ge, Ti, Fe, (Bi, Ga), (Bi, Fe), (Bi, Zn), (Bi, V). In single crystals of solid solutions with the fluoride-related structure the known clusters Li4F26 or Lu4F26 are formed, depending on the relation of ionic radii of M3+ and R3+ cations. If a large number of M3+ cations are replaced by R3+ cations, more complex clusters are formed with a simultaneous probable accommodation of complementary P3+ cations on the two and three-fold 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, 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 Bi3+. In fact, in this case MO4 tetrahedra 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 BiO4 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 bilability of sillenite framework is so great that Fe3+ and P3+ cations with totally different ionic radii are allowed to occupy statistically the M site. The unusually remarkable isomorphism of cations in fluorites and silenites permits controlled changes of physical properties of these compounds.

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STRUCTURE RELATIONSHIPS
Chenlistry Chemistry Communications, Uppsala University, Sweden

References:

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+[4+2]-COORDINATED MOLYBDENUM IN THE CHAIN STRUCTURE OF Rb2Cu2(MoO4)3
S.P. Solodovnikov, Z.A. Solodovnikova, V.I. Alekseev, Institute of Inorganic Chemistry, Novosibirsk, Russia

The atomic arrangement of Rb2Cu2(MoO4)3 with a new structure type was determined. The main features of the structure are the following: (i) couples of infinite wolfenite-like ribbons of CuO4+2- octahedra running along [010] and sharing vertices with two topologically different types of bridging MoO4-tetrahedra (fig.), (ii) the tetradentate MoO4-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 niobium atoms. The new structure type represented by A2Cu2(MoO4)3 (A = Rh, Cs) only completes the morphotropic series of double molybdates A2M2(MoO4)3 (A = K, Rh, Cs, Tl; M = Mg, Mn, Co, Ni, Cu, Zn, Cd) which were known to possess the structures of K2Zn2(MoO4)3, K2Mn2(MoO4)3 or K2Mg2(SO4)3 (langbeinite). The substantial difference of the Rb2Cu2(MoO4)3 type with a chain structure from the other structures containing frameworks of M4O8-octahedra and MoO4-tetrahedra seems to be caused by stereochemical peculiarities of Cu(II).

Synthesis: the light green needle-like crystals were obtained by slow crystallization of the mixture CuMoO4 + Rb2MoO4 from 650 to 400°C at cooling rate of 5ºC/h.

Crystal data: monoclinic, sp. gr. C2/c, a=27.698(2), b=5.102(1), c=19.292(1) Å, β=107.26(1)º, Z=8, λMoKα, R=0.016 for 882 1>0.

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).

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PSEUDO-SYMMETRY IN STRUCTURE OF Re6XY4+
N. L. Speziali and C. B. Pinheiro, Departamento de Fisica, ICEx - UFMG, Belo Horizonte - Brazil

A number of compounds presenting rhenium octahedral clusters in their structures have been investigated and related to Chevrel phase to molybdenum compounds. The ternary compounds Re6XY4+ (Y=Cl, Br and X=Se, S) crystallize with well defined clusters of Re6L6 (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 Re6XY4+ family have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state). The 18 number of compounds presenting rhenium octahedral clusters in their structures have been investigated for different type and number of inter-cluster atoms. The 12 d4 state single-covalent-Re-Re bonds envolves 24 of 42 valence electrons (6 Re atoms in 4f145d56s2 state).