

BaCu₂S₂ is a representative of a chalcogenide group with the ThCr₂Si₂-type layer structure. The way of synthesizing the tetragonal modification of BaCu₂S₂ with: $a=3.909$, $c=12.655$ Å parameters has been suggested in the paper (Saeki M., Onoda M., Nozaki H., Mater. Res. Bull., 1988, 23, 4, 603); a crystal structure determination of BaCu₂S₂ obtained by another way and compounds with potassium and rubidium inserted into this structure was undertaken in our work (Saveliyeva M., V., Alekseev V. I. et al., Izv. SO AN SSSR. Rhim. Sek. 1990, 1, 123-125).

For X-Cu-M-S system (X=K, Rb, Cs, M=Fe, Mn, Zn) we have managed to obtain a series of compounds with general formula X₂Cu₃MS₄ (X=K, Rb, Cs, M=Fe) one of them-K₂Cu₃FeS₄ is known (Dobrovolskaya M. G. et al. Zap. Un. Min. Soc., 1981, 4, 468-473) as mineral Murunskit, however without any structure investigations. For X=K, Rb, Cs, M=Mn, Zn we have obtained compounds with a general formula XCuMnS₂. In both cases the structure supposes to be of the ThCr₂Si₂-type, that is typical for transition metal chalcogenides AM₂X₂ (A=K, Rb, Cs, M=Co; A=K, M=Ni, X=S, Se) (Huan G. et al., Eur. J. Solid State Inorg. Chem., 1989, 26, 193). All samples were prepared in the atmosphere of CS₂ at 900±50°C from Cu₂O, the corresponding metal oxide (ZnO, Fe₂O₃, MnO₂) and Rb₂CO₃, Cs₂CO₃, KHCO₃, which were taken in definite stoichiometry. Chemical composition of the products was estimated by chemical and powder X-ray diffraction analysis. A granulometric investigation of particles was carried out on a SK laser micron sizer "PRO-7000". The melting points of compounds were determined by DTA method. The temperature variations of resistivity were measured by conventional four-probe technique on pressed pellets sintered at 850°C.

The proximity of the tetragonal unit cell parameters of samples and appearances of their diffraction patterns (DRON-UM1, R=192mm, CuKα-radiation, Ni-filter, Si-external standard) indicates a retaining of the ThCr₂Si₂-type structure.

PS-08.04.45 CRYSTAL STRUCTURE OF TETRAPOTASSIUM PENTAMOLYBDODISELENIUM(IV) DIHYDRATE K₄NaSe^{IV}₂Mo₆O₂₁·2H₂O
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Selenium is one of the essential elements and is required for almost all forms of life. Some heteropolyanions of selenium are described but a few crystal structure information is available.

The structure of the Strandberg-type heteropolymolybdate of selenium K₄NaSe^{IV}₂Mo₆O₂₁·2H₂O has been determined by the single-crystal X-ray method.

Crystal data:

Monoclinic, space group P-2₁/n, $a=9.851(2)$, $b=23.224(6)$, $c=10.456(3)$ Å, $\beta=114.13(2)^\circ$, $V=2183.1$ Å³, and $Z=4$. The structure was refined by full-matrix least squares to $R=0.069$ for 2845 reflexions with $F_o>5\sigma(F)$

The [Se^{IV}Mo₆O₂₁]⁴⁻ anion has the distinguishable pentagonal molybdate framework of MoO₆ octahedra, which are joined together through four sharing of edges and one corner sharing approximating a plane to form a Mo₆O₂₁ pentagon. The two Se^{IV}O₃ trigonal pyramids are situated so that the Mo₆O₂₁ pentagon is capped on both sides of the plane.

PS-08.04.46 CRYSTAL STRUCTURE OF A REMARKABLE POLY-METALLATE OXYGEN CLUSTER [H₂Mo₂₇Fe^{IV}₁₂O₁₂₆(NO)₆(H₂O)₁₂(MoO₄)]⁸⁻
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Understanding the driving force for the formation of high nuclearity clusters is still a formidable challenge. We recently reported the structure with the largest polymetallate cluster involving mixed valence molybdenum and vanadium(IV) or iron(III) (Zhang, Huang, Shao & Tang, J. Chem. Soc., Chem. Commun., (1993), 1, 37). Here is another remarkable cluster structure with mixed valence molybdenum and iron(II). They may give an indication about the possible mechanism of formation of the polymolybdate.

Crystal data:

Hexagonal, space group P-6₃/mmc, $a=23.868(5)$ Å, $c=27.521(12)$ Å, $V=13577$ Å³ and $Z=2$. The structural parameters have been refined to convergence $R=0.058$ for 2067 reflexions with $F_o>4.0\sigma(F)$.

The interesting cluster consists of three 17-molybdate subunits related to each other by a three-fold axis; the cluster centre sits on a special position with 6m2 crystallographic symmetry, and each individual subunit has internal C_{2v} symmetry.

Each subunit contains fifteen MoO₆ octahedra and two MoO₆(NO) pentagonal bipyramids in which the oxidation state of Mo atom is 5⁺; three subunits are connected by six Fe^{IV}O₆ octahedra and six MoO₆ octahedra linked by six bridging water molecules and three bridging oxygen atoms. In central cavity, there are 12 water molecules, which are situated around $\bar{6}$ fold axis and coordinated to six molybdate and six iron(II) respectively; moreover, these 12 water molecules are linked to each other by hydrogens bonding to form two six-membered rings.

There are still two four-coordination Mo atom occupying the six outer cavities of the cluster with 1/3 probability. Such occupancies for Mo atoms can be explained by the fact that the anion with high negative is stabilized by two (MoOH)⁶⁺ groups and the cavity is a good room to accommodate the tetrahedra.

PS-08.04.47 MIXED VALENT MOLYBDENUM PHOSPHATES INVOLVING Mo(V). By A. Leclaire*, M.M. Borel, A. Grandin and B. Raveau. CRISMAT, CNRS-URA1318, Caen France.

A large series of molybdenum phosphates has been isolated during these last ten years with a molybdenum valency ranging from III to VI. In most of these phosphates, molybdenum exhibits an octahedral coordination. The different valences can be present in the same framework leading to compound with a mixed valency for molybdenum. The most frequent mixed valences involve Mo(III) and Mo(IV). They have been synthesized and studied principally by R.C. Haushalter and al., by Lii and al. and by the authors. In these compounds each valency has generally its own well defined sitting, for instance in NaMo₂P₄O₁₄ the two independent sites for molybdenum contain respectively Mo(III) and Mo(IV). In the other hand very few mixed valent molybdenum phosphates involving Mo(V) have been synthesized. Only six kinds of frameworks corresponding to the phosphates: AMo₂P₂O₁₀·xH₂O and Cs₆Mo₇P₇O₃₇·H₂O characterized by the mixed valences Mo(IV)/Mo(V) Cs₃Mo₄P₄O₂₂ and Rb₃Mo₄P₄O₂₂ and AMo₃P₃O₁₆ and KMo₃P₂O₁₄ characterized by the mixed valency Mo(V)/(Mo(VI)) are known up to now. This rarity may be related to the particular configuration of Mo(V) which tends to form molybdenyl ions and would prevent a delocalisation of the electrons in the structure.

The first mixed valent molybdenum phosphate involving Mo(IV) and Mo(V) isolated by R.C. Haushalter and al. using hydrothermal synthesis was NH₄Mo₂P₂O₁₀·H₂O. This compound is isotopic with leucophosphate, it exhibits tetraoctahedral units built up from two edge-sharing Mo(IV)O₆ octahedra which share also one of their corners with one Mo(V)O₆ octahedron. These units are linked together by PO₄ tetrahedra. The polyhedra delimit large intersecting tunnels. We have synthesized by solid state chemistry isotopic compounds