Supramolecular oxometalate chemistry: octamolybydate as a building block.

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Octamolybdate has been found to form two kinds of complexes with trivalent lanthanum cations: [La(MoO₄)₂]²⁻ and [La₂(NO₃)₆(MoO₄)₂]⁺. In the former, whose analogue can also be prepared for Y, Ce, Pr, Nd, Gd and Yb, the coordination sphere of lanthanum is completed square anti-prismatically by 8 oxometalate oxygen atoms of the two [MoO₄]³⁻ moieties, thus forming a dimeric oxometalate linked to each other via the La³⁺ cation. In the latter, nitrate anions coordinate to the La³⁺ cation to terminate further polymerization. So this anion was only synthesized for La, Ce and Pr, indicating that the heavier lanthanide elements with smaller ionic radii cannot accommodate octamolybdate and nitrate anions simultaneously. These two polyoxometalate complexes show the potential to compose supramolecular oxometalate complexes utilizing octamolybdate as building blocks and the lanthanide cations as the glue.

H₂(AsF₆)₂ polyhedra and (Hg₂)²⁺ dumbbells are responsible for structural peculiarities of these compounds. The Hg²⁺ is coordinated two oxygen atoms and the Hg distance of 2.98 Å in terlinguaitite, however, the Hg²⁺ is coordinated two oxygen atoms of the two [MoO₄]³⁻ moieties, thus forming a dumbbell chain. The Hg-Hg bond lengths were found to be 2.71 Å, suggesting that this structural fragment involves a mixed-valent property of mercury, due to its electron shell structure. The capacity for forming linear anisotropic triangles with the Hg-Hg distances of 2.46-2.64 Å, is bonded to the other tetrad at the shape of reciprocal lattice points.

In the Mg₂ rich end of the crystal (wurtzite type, x=0.25 determined by EPMA) the 4H phase is not detected and the amount of 4H is considerable. Due to the lack of pure 4H phase, the structural information was obtained by Rietveld refinement of the mixture of wurtzite and 4H. For x=0.21, the lattice constants of 4H are c=4.041, a=13.214. The 4H polytype is known in other II-VI systems, e.g. in Cu₂ZnS and Zn₂(Se,S) crystals grown by the same method [4]. The polytypism in both (Zn,Mg)Se and Zn₂(Se,S) ternaries implies the need for studies of the possible polytypes formation in quaternary (Zn,Mg)₂(Se,S)₉, a component of heterostructures considered for use in blue light emitting diodes and lasers, in order to explain the degradation processes in such electroluminescent devices.

Using four-circle diffractometer and Buerger precession camera with an image plate the structure of Bridgman grown single crystals of stoichiometric and nickel rich (x = 0.08) Ni₆ZnAl₃Se₆ (Pm-3m) has been refined. Moreover, samples were deformed plastically at 800 - 900 °C.

Lattice parameters obtained from 120 reflections agree with literature values at room temperature [1-3]. In addition data between 120 and 320 K have been obtained for both lattice parameters a and thermal expansion coefficients α. These are for x = 0: a = 2.8872(2) Å at r.t. and α = 1.4(2) ± 10⁻⁴ K⁻¹ between 120 and 320 K; for x = 0.08: a = 2.8792(2) Å.

Refinement of size occupancy factors on integrated intensity data leads to Ni on Al positions for the nickel rich sample (s.o.f. g=0.08). Using four-circle diffractometer and Buerger precession camera with an image plate the structure of Bridgman grown single crystals of stoichiometric and nickel rich (x = 0.08) Ni₆ZnAl₃Se₆ (Pm-3m) has been refined. Moreover, samples were deformed plastically at 800 - 900 °C.

X-ray single crystal diffraction investigation on Ni₆ZnAl₃Se₆. P. Paulsen, J. Faber, G. Zahn, Institut für Kristalllographie und Festkörperphysik, Technische Universität Dresden, D 01062 Dresden, Germany.

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