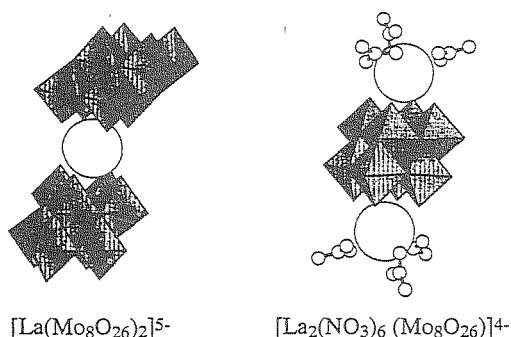


PS08.00.31 SUPRAMOLECULAR OXOMETALATE CHEMISTRY: OCTAMOLYBDATE AS A BUILDING BLOCK. Tomoji Ozeki^a, Akira Kitamura^b and Atsushi YAGASAKI^b ^aDepartment of Chemistry, Faculty of Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152, Japan and ^bDepartment of Chemistry, School of Science, Kwansai Gakuin University, Uegahara, Nishinomiya 662, Japan

β -Octamolybdate has been found to form two kinds of complexes with trivalent lanthanum cations: $[\text{La}(\text{Mo}_8\text{O}_{26})_2]^{5-}$ and $[\text{La}_2(\text{NO}_3)_6(\text{Mo}_8\text{O}_{26})]^{4-}$. 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 $[\text{Mo}_8\text{O}_{26}]^{4-}$ moieties, thus forming a dimeric octamolybdate linked to each other via the La^{3+} cation. In the latter, nitrate anions coordinate to the La^{3+} cation to terminate further polymerization. So far 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.



PS08.00.32 CRYSTAL CHEMISTRY OF MERCUROS INORGANIC COMPOUNDS AND MINERALS. N.A. Pal'chik, S.A. Magarill, L.M. Volkova. Institute of Geology Sib. Branch RAS, Novosibirsk, Russia; Institute of Inorganic Chemistry Sib. Branch RAS, Novosibirsk, Russia; Institute of Chemistry FE Branch RAS, Vladivostok, Russia

An unique property of mercury, due to its electron shell structure, is the capacity for forming linear Hg_n ($n=2,3,4,\infty$) systems with the Hg-Hg distance of 2.46-2.64 Å. The Hg-Hg bond lengths were found to be dependent on n : in Hg_2 dumbbell 2.46-2.54, in Hg_3 chain 2.55, for Hg_4 2.58-2.62, and in Hg_∞ infinite chain 2.64 Å. In these systems, Hg has the formal valency from +1 to +0.3. In terlinguaite and kusnetsovite minerals, mercury atoms form planar triangles with the Hg-Hg distances of 2.71 and 2.64 Å, respectively. In the triangles, the formal valency of Hg is +1.33, suggesting that this structural fragment involves a mixed-valent mercury atom. In terlinguaite, however, the Hg^{2+} is coordinated two oxygen atoms and the Hg-Hg distance to the nearest mercury atom of the triangle is more than 3 Å. Similarly, in the structure of wattersite, Hg_2^{2+} polyhedra and $(\text{Hg}_2)^{2+}$ dumbbells are at a distance of >3 Å. The $\text{Hg}_4(\text{AsF}_6)_2$ structure is also of interest in that a linear $(\text{Hg}_4)^{2+}$ tetrad (with the distances 2.58-2.62 Å) is bonded to the other tetrad at the Hg-Hg distance of 2.98 Å to form an infinite polymer with the chain charge +0.5.

A relation between conducting and other physical properties and structural peculiarities of these compounds is discussed in this report. As an example, in the Hg_3AsF_6 structure, infinite Hg-Hg chains (2.64 Å), running in two mutually perpendicular nonintersecting directions, are responsible for anisotropic superconductivity. Crystal chemical properties

of these minerals and inorganic compounds will allow an understanding and an explanation for their physical properties, crystallization conditions, as well as modelling the basic skeleton of new minerals and compounds and predicting their physical properties.

PS08.00.33 H-POLYTYPE FORMATION IN $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$. W. Paszkowicz¹, Z. Spolnik¹, F. Firszt² and H. Méczyńska², ¹Institute of Physics, P.A.S., al. Lotników 32/46, Warsaw, Poland, ²Inst. of Physics, N.Copernicus University, Grudziadzka 5, Toruń, Poland

$\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ thin layers have been reported to adopt the sphalerite structure type of the substrate for $0 < x \leq 0.5$ [1]. X-ray studies of bulk $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ crystals grown in the range $0 < x < 0.56$ by the Bridgman method [2,3] have shown that above $x=0.2$ the structure is of the wurtzite type rather than of the sphalerite type. Powder X-ray analysis of a new crystal prepared from a mixture of pure ZnSe, Mg and Se reveals the presence of the 4H polytype. In the Mg-rich end of the crystal (wurtzite type, $x=0.25$ determined by EPMA) the 4H phase is not detected while at the other end 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 $a=4.041$, $c=13.214$. The 4H polytype is known in other II-VI systems, e.g. in $(\text{Cd,Zn})\text{S}$ and $\text{Zn}(\text{Se,S})$ crystals grown by the same method [4]. The polytypism in both $(\text{Zn,Mg})\text{Se}$ and $\text{Zn}(\text{Se,S})$ ternaries implies the need for studies of the possible polytypes formation in quaternary $(\text{Zn,Mg})(\text{Se,S})$, 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.

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PS08.00.34 X-RAY SINGLE CRYSTAL DIFFRACTION INVESTIGATION ON $\text{Ni}_{1+x}\text{Al}_{1-x}$. P. Paufler, J. Faber, G. Zahn, Institut für Kristallographie und Festkörperphysik, Technische Universität Dresden, D 01062 Dresden, Germany

Using four-circle diffractometer and Buerger precession camera with an image plate the structure of Bridgman grown single crystals of stoichiometric and nickel rich ($x = 0.08$) $\text{Ni}_{1+x}\text{Al}_{1-x}$ (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 $\alpha = 1.4(2) \cdot 10^{-5}$ K⁻¹ between 120 and 320 K; for $x = 0.08$: $a = 2.8798(2)$ Å.

Refinement of size occupancy factors on integrated intensity data leads to Ni on Al positions for the nickel rich sample (s.o.f. $\text{Ni}_{\text{Al}} = 0.074(10)$). This agrees well with results taken from electron beam microanalysis ($x = 0.078(23)$). Buerger precession exposures were taken from deformed crystals in order to analyze the shape of reciprocal lattice points.

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