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energy that separates the bonding & antibonding orbitals if one allows the formation of Hg dimer metal to Hg on the ground that Hg has the configuration [Xe] 4f^{14} 5d^{10} 6s^2. Details of the semiquantitative calculations will be presented.

PS-08.04.07 TERNARY NIOBIUM CHALCOGENIDE HALIDES: PREPARATION AND CHARACTERIZATION OF Nb_xS_x AND (Nb_xS_x)2Nbf. By J. Lin and G. J. Miller, Department of Chemistry and Ames Laboratory-USDOE, Iowa State University, USA.

It has been shown that most of the Nb_xY_x (Y = Chalcogen, X = Halogen) compounds adopt the Nb_xY_x layer structure (G. J. Miller, unpublished). The niobium atoms fill 3/8 of the octahedral holes of a close packed array of anions to form sandwich-type layers. A basic structural feature of this layer is that the niobium atoms form triangular clusters by sharing octahedral edges. All of these compounds crystallize in either hexagonal or trigonal symmetry depending upon the stacking sequences of the layers. In the Nb-S layer, in addition to the hexagonal phase, an orthorhombic Nb_xS_x as well as a new compound, (Nb_xS_x)2Nbf, were found.

All of the compounds were synthesized from elemental materials and characterized by single crystal X-ray diffraction. The crystals of (Nb_xS_x)2Nbf were always found as twins, so the structure was refined with a twin program SFLS. The twin operation is (1 0 0) (0 1 0) (1 6 0 1).

The anion array in the orthorhombic Nb_xS_x structure is cubic close packing. The niobium atoms occupy the octahedral holes in the sequence [AeB]_2[Re2B]_x[Re2A]_y[AeC]. A, B and C, a, b and c, represent, respectively, the anion arrays, niobium arrays 5/8 filled and 1/8 filled sites of octahedral holes. The niobium triangular clusters in this structure are formed either within or between layers of metal atoms. The whole structure is also layered, but the sheets are buckled and run perpendicular to the c axis.

Fig. 1. Projection of the (Nb_xS_x)_2(Nbf) structure along c.

In the monoclinic (Nb_xS_x)2Nbf structure, the niobium atoms form the triangular cluster via sharing octahedral faces and each cluster connects with three other clusters by sharing edges to form a layer with large hexagonal holes, as shown in Fig. 1. The whole framework is constructed by stacking these layers one over another along c to achieve a chain-like structure. The isolated Nb_1 molecule with trigonal bipyramidal geometry sit at the positions between the layers along the channels. We should point out that in the solid state, Nb_3 occurs with the niobium atoms in octahedral coordination and polymerized into Nb_7 oligomer. The trigonal bipyramidal coordination of niobium is known in the gas phase of NbCl and in some niobium oxides. Extended Hückel band calculations show that this geometry increases the energy gap between the HOMO and LUMO, so as to reduce the electron transfer from the framework to Nb_3 molecules.

PS-08.04.08 STRUCTURAL CHANGES IN ISOSTOICHIOMETRIC SERIES OF ALKALI LANTHANUM NITRATES. By A.G. Vidorchik, Yu.A. Malinovsky, Institute of Crystallography Russian Acad. of Sci., Lenininsky pr.59, Moscow, 117333, Russia.

Our investigation was performed in the course of a systematic study of alkali rare-earth nitrates and is devoted to an analysis of the structural crystal - chemical characteristics of isostoiometric series of alkali lanthanum nitrates A_2La(NO_3)_4(H_2O)_4 NH_3, where A = Cs, Rb, NH_4, K. Such a comparative analysis shows how far the nature of the alkali metals influences the structure of these compounds. The Cs, Rb, and ammonium compounds have similar values of the unit cell parameters. We can note their similarity both in the structure of the rare-earth complexes and in the packing of these complexes in the structure. The only essential difference lies in the absence of water molecules outside the coordination sphere of the La atoms in the cesium compound. The channels in which the alkali ions lie have approximately equal dimensions. The cavities adequate for the Cs atoms are too ample for the smaller Rb* and NH_4* ions. This circumstance determines the possibility of water getting into the intraframework cavities of the rubidium and ammonium compounds. The ammonium ions tend to form hydrogen bonds. They join the ammonium ions and the molecules of intermolecular water to form the chains along A axis. Thus, why the ammonium ions are fixed in one position, while the Rb atoms occupy statistically two independent positions. The organization of the structure of K_2La(NO_3)_4(H_2O)_4 is quite different as the ionic radii of cesium, ammonium and rubidium are too large in comparison with potassium.

PS-08.04.09 CRYSTAL STRUCTURE OF PEROXOKTITIC KGeO_4 CRYSTALS. By M.I. Sorokin, V.I. Verin, V.I. Simonov, Institute of Crystallography, Moscow, Russia; V.V. Voronkov, V.K. Zosimov, Physics Department, Moscow State University, Russia.

Single crystals of KGeO_4 (KGO) which belong to the family of ferroelectric and nonlinear optical compounds of the KTiOPO_4 (KTP) type have been obtained. Their dielectric susceptibility has been measured and their crystal structure has been studied. The ferroelectric phase transition temperature for KGO is 795°С which is close to the temperature of incongruent melting of this compound at 808°С. Besides, relaxation phenomena due to a high ionic conductivity are observed. The KGO crystals at room temperature have the polar esp.gr. Pnm, with the following unit cell parameters: a=12.6011(10), b=10.399(5), c=10.0011(3) Å. Our 3-ray structural study (neutron- and X-ray- on orientation determinations) shows that the crystal structure is triclinic (P-1) with the following cell parameters: a =6.1253(10), b = 7.980(4), c = 9.625(5) Å, α = 95.650(2), β = 101.800(2), γ = 92.950(2)°. The space group is P1. The space group is P1. The space group is P1.