80-Inorganic and Mineralogical Crystallography

energy that separates the bonding & antibonding orbitals if one considers the formation of H₂ dimers to H₂O. It was noticed that H₂O has the configuration [Xe] 4d² 5s² 5p⁶ 6s². Details of the semi-quantitative calculations will be presented.

PS-08.04.07 TERNARY NIOBIUM CHALCOGENIDE HALIDES: PREPARATION AND CHARACTERIZATION OF Nb₅SₓIₓ AND (Nb₅S₃)ₓNb₅Iₚ. 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shown that most of the Nb₅XY (Y = Chalcogen, X = Halogen) compounds adopt the Nb₅X₈ layered structure (G. J. Miller, unpublished). The niobium atoms fill 3/8 of the octahedral holes of a close packed array of atoms 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 S₅-I system, in addition to the hexagonal phase, an orthorhombic Nb₅S₃Iₚ as well as a new compound, (Nb₅S₃)ₓNb₅Iₚ, were found.

All of the compounds were synthesized from elemental materials and characterized by single crystal X-ray diffraction. The crystals of (Nb₅S₃)ₓNb₅Iₚ were always found as twins, so the structure was refined with a twin program SFLS. The twin operation is (1 0 0) 8 (1 0 0) 8 (0 1 0). The scattering factors for Nb and S are taken from the International Tables for X-ray Crystallography.

The orthorhombic Nb₅S₃Iₚ structure is cubic close packing. The niobium atoms occupy the octahedral holes in the sequence [Nb₂S₃]²⁺[Nb₂S₃]²⁺[Nb₂S₃]²⁺[Nb₂S₃]²⁺[Nb₂S₃]²⁺[Nb₂S₃]²⁺[Nb₂S₃]²⁺[Nb₂S₃]²⁺. The niobium atoms form triangular clusters with Nb₅ molecules. The cluster is also layered, but the sheets are buckled and run perpendicular to the c axis.

![Fig. 1. Projection of the (Nb₅S₃)ₓ(Nb₅Iₚ) structure along c.](image)

In the monoclinic (Nb₅S₃)ₓ(Nb₅Iₚ) 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 channel-like structure. The isolated Nb₅ molecules with trigonal bipyramidal geometry sit at the positions between the layers along the channels. We should point out that in the solid state, Nb₅ occurs with the niobium atoms in octahedral coordination and dimerized into Nb₁₀ cluster. The trigonal bipyramidal coordination of niobium is known in the gas phase of NbCl₅ 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 Nb₅ molecules.

PS-08.04.08 STRUCTURAL CHANGES IN ISOOSTOICHIOMETRIC SERIES OF ALKALI LANTHANUM NITRATES. By A.G. Vydorovich, Yu.M. Malinovsky, Institute of Crystallography Russian Acad. of Sci., Leninskly 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 isoosticomicetric series of alkali lanthanum nitrates.

A₁-La(NO₃)ₓ{H₂O,y}·nH₂O, where A = Cs, Rb, NH₄, 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 in the coordination sphere of the La atoms in the ammonium 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 NH₄⁺ ions. This circumstance determines the possibility of water getting into the intraskeletal cavities of the rubidium and ammonium compounds. The ammonium cations tend to form hydrogen bonds. They join the ammonium ions and the molecules of intermolecular water to form the chains along the c axis. This is why the ammonium ions are fixed in one position, while the Rb atoms occupy statistically two independent positions. The organization of the structure of K₁-La(NO₃)ₓ{H₂O,y}·nH₂O 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 FERROELECTRIC KGeO₄ CRYSTALS. By N.I. Sorokin, I.A. Verin, V.I. Simanov, Institute of Crystallography, Moscow, Russia; V.I. Yurkov, V.K. Kuznetsov, Physics Department, Moscow State University, Russia.

Single crystals of KGeO₄ (KGO) which belong to the family of ferroelectric and nonlinear optical compounds of the 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 76°C which is close to the temperature of incongruent melting of this compound at 83°C. Besides, relaxation phenomena due to a high ionic conductivity are observed. The KGO crystals at room temperature have the polar sp. gr. Pm3m, with the following unit cell parameters: a=12.601±(10), b=10.395±(5), c=10.051±(8) Å. Our 3-ring neutron study (an "Enraf-Nonius" auto diffractometer, AgKα, radiation,