

## 08-Inorganic and Mineralogical Crystallography

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energy that separates the bonding & antibonding orbitals if one likens the formation of Hg dimer moiety to H<sub>2</sub> on the ground that Hg<sup>2+</sup> has the configuration [Xe] 4f<sup>14</sup> 5d<sup>10</sup> 6s<sup>1</sup>. Details of the semiquantitative calculations will be presented.

**PS-08.04.07 TERNARY NIOBIUM CHALCOGENIDE HALIDES: PREPARATION AND CHARACTERIZATION OF Nb<sub>3</sub>SI<sub>7</sub> AND (Nb<sub>3</sub>SI<sub>7</sub>)<sub>2</sub>NbI<sub>5</sub>.** 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<sub>3</sub>YX<sub>7</sub> (Y = Chalcogen, X = Halogen) compounds adopt the Nb<sub>3</sub>X<sub>8</sub> layer structure (G. J. Miller, unpublished).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-I system, in addition to the hexagonal phase, an orthorhombic Nb<sub>3</sub>SI<sub>7</sub>, as well as a new compound, (Nb<sub>3</sub>SI<sub>7</sub>)<sub>2</sub>NbI<sub>5</sub>, were found.

All of the compounds were synthesized from elemental materials and characterized by single crystal X-ray diffraction. The crystals of (Nb<sub>3</sub>SI<sub>7</sub>)<sub>2</sub>NbI<sub>5</sub> 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<sub>3</sub>SI<sub>7</sub> structure is cubic close packing. The niobium atoms occupy the octahedral holes in the sequence [AcBa<sup>+</sup>CbAc<sup>+</sup>BaCb<sup>+</sup>Ac]. A, B and C, a, b and c, as well as a<sup>+</sup>, b<sup>+</sup> and c<sup>+</sup> 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  $\vec{c}$  axis.

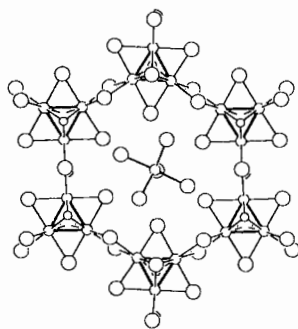


Fig. 1. Projection of the (Nb<sub>3</sub>SI<sub>7</sub>)<sub>2</sub>(NbI<sub>5</sub>) structure along  $\vec{c}$ .

In the monoclinic (Nb<sub>3</sub>SI<sub>7</sub>)<sub>2</sub>NbI<sub>5</sub> structure, the niobium atoms form the triangular cluster by 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  $\vec{c}$  to achieve a channel-like structure. The isolated NbI<sub>5</sub> molecules with trigonal bipyramid geometry sit at the positions between the layers along the channels. We should point out that in the solid state, NbI<sub>5</sub> occurs with the niobium atoms in octahedral coordination and dimerized into Nb<sub>2</sub>I<sub>10</sub> cluster. The

trigonal bipyramidal coordination of niobium is known in the gas phase of NbCl<sub>5</sub> 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 NbI<sub>5</sub> molecules.

**PS-08.04.08 STRUCTURAL CHANGES IN ISOSTOICHIOMETRIC SERIES OF ALKALI LANTHANUM NITRATES.** By A.G.Vigdorchik\*, Yu.A.Malinovsky, Institute of Crystallography Russian Acad. of Sci., Leninsky 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 isostoichiometric series of alkali lanthanum nitrates A<sub>2</sub>[La(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>H<sub>2</sub>O, where A = Cs, Rb, NH<sub>4</sub>, 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<sup>+</sup> and NH<sub>4</sub><sup>+</sup> ions. This circumstance determines the possibility of water getting into the intraframework cavities of the rubidium and ammonium compounds. The ammonium ion tends to form hydrogen bonds. They join the ammonium ions and the molecules of intermolecular water to form the chains along Y axis. That 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 K<sub>2</sub>[La(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)<sub>2</sub>] 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 KGeOPO<sub>4</sub> CRYSTALS.** By N.I.Sorokina\*, I.A.Verin, V.I.Simonov, Institute of Crystallography, Moscow, Russia; V.I.Voronkova, V.K.Yanovskii, Physics Department, Moscow State University, Russia.

Single crystals of KGeOPO<sub>4</sub> (KGP) which belong to the family of ferroelectric and nonlinear optical compounds of the KTiOPO<sub>4</sub> (KTP) type have been obtained. Their dielectric susceptibility has been measured and their crystal structure has been studied. The ferroelectric phase transition temperature for KGP is 785°C which is close to the temperature of incongruent melting of this compound at 805°C. Besides, relaxation phenomena due to a high ionic electroconductivity are observed. The KGP crystals at room temperature have the polar sp.gr. Pna2<sub>1</sub> with the following unit cell parameters: a=12.6013(10), b=6.3051(5), c=10.0031(8) Å. Our X-ray structural study (an "Enraf-Nonius" autodiffractometer, AgK<sub>α</sub>-radiation,