

PS08.00.18 SUPERSTRUCTURES IN THE VANADIUM CONTAINING BISMUTH OXIDES. S. Kashida, A. Kuwasawa and T. Saito, Faculty of Science, Niigata University, Ikarashi, Niigata, 950-21, Japan

Bismuth sesquioxide has attracted wide interest as fuel cell materials. It is an excellent oxygen ion conductor in its high temperature phase. This high temperature fluorite phase is apparently stabilized to room temperature, by doping transition metal oxides. Recent electron diffraction and high resolution electron microscopic studies have disclosed a variety of phases in these 'stabilized bismuth oxides' [W. Zhou, J. Solid State Chem, 76, 290 (1988)].

Using single crystal X-ray diffraction method, we have investigated the structure in the $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ system. This system shows a sequence of cation ordering phases. Vanadium atoms occupy the cation sites, starting from each at far neighbor sites, since the vanadium-vanadium interaction is of Coulombic and will be repulsive. The $9\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ compound has a $3\times 3\times 3$ superstructure derived from the fluorite cell. Vanadium atoms are located at every third layer along the [111] axis. In the layer they occupy the third neighbor cation sites. Oxygen vacancies are concentrated at nearest neighbor sites of vanadium ions.

The $6\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ compound has a pseudo monoclinic structure. The lattice is represented using the fluorite cell as, $a=3/2(1,1,2)$, $b=3/2(-1,1,0)$, $c=1/2(-5,-5,2)$ and $\beta=107.13$. The structure is composed of six (111) layers stacked along the c-axis, each containing 18 metal atoms. The cation arrangement can be expressed by the number of vanadium atoms as 4-0-4-4-0-4. The lattice has square wave type displacements (0.6\AA) along the b-axis. The large displacements are attributed to the electrostatic repulsion between vanadium atoms in the nearest neighbor cation sites. A long period trilling structure with 21 (111) layers was observed around the composition $\text{Bi}_2\text{O}_3\text{:V}_2\text{O}_5=9\text{:}1$. A microscopic model is presented for this trilling structure, where vanadium atoms come to the nearest neighbor sites at every seven layer and share oxygen vacancies in common.

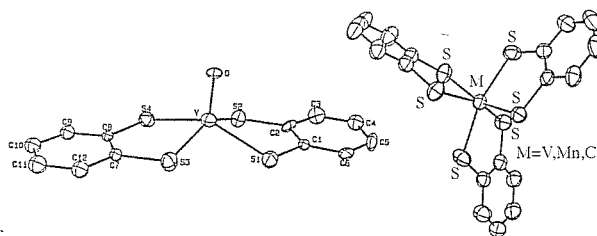
PS08.00.19 HYDROGEN ATOMS LOCALIZATION FROM COMPARISON OF DIFFRACTION AND PMR SPECTROSCOPY DATA. Valery Kavun, S.G.Kozlova¹ and S.P.Gabuda¹. Institute of Chemistry, 690020, Vladivostok, Russia; ¹Institute of Inorganic Chemistry, 630090 Novosibirsk, Russia

Neutron diffraction study of zeolite single crystals revealed the unusual shortening of intramolecular H-H distances for adsorbed H_2O molecules. The shortest ones are 1.42\AA in edingtonite, 0.76\AA in yugovalarite, 0.84\AA in heulandite. All these data do not consist with well established intramolecular water parameters both for gas phase (1.515\AA) and for condensed phase (ice I - 1.54\AA , water in gypsum - 1.56\AA , water in narrow-pored zeolite natrolite - 1.56\AA and so on). According to Busing and Levy (*Acta Cryst.* 17,142,1964), above distortion of bond lengths data indicates that thermal motion, or orientational disordering of water molecules takes place. This mechanism is supported by neutron diffraction study of the crystal structure of zeolite laumontite, where was established the "highest degree of disorder of the water molecules" among zeolites well characterized by neutron diffraction. But still there is no generally accepted ways how to account this effect and to correct the distorted bond length data deduced from diffraction measurements.

We propose an approach which is based on the use of the proton magnetic resonance (PMR) data. The correct interproton distances and amplitudes of both thermal motion or disordering parameters can be calculated from comparison of two independent data sets: (1) diffraction ones, (2) PMR spectroscopy. As illustration of fitness of proposed method we regarded the hydrogen atoms localization in potassium hexafluorostannate monohydrate and in hemimorphite single crystals, using own PMR and X-ray diffraction data for $\text{K}_2\text{SnF}_6\cdot\text{H}_2\text{O}$, and own PMR and previous neutron diffraction data on hemimorphite.

PS08.00.20 STRUCTURAL ASPECTS OF TRANSITION METAL BENZENEDITHIOLATO COMPLEXES. Kristin Kirschbaum, Armin Corbach, Arnold Feldmann, Klaus Laue, Dirk Pfeiffer and Dean M. Giolando, Department of Chemistry, University of Toledo, Toledo, Ohio, 43606-3390.

The coordination chemistry of transition metals containing a homoleptic thiolate environment is of general interest. We have been investigating the structural chemistry of complexes with 1,2-benzenedithiolate ligands. Three bis(1,2-benzenedithiolate)vanadyl complexes have been prepared: $[\text{N-}i\text{-Bu}_4]_2[\text{VO}(\text{S}_2\text{C}_6\text{H}_4)_2]$ (1a) monoclinic, $P2_1/n$, $Z=4$, $a=15.579(4)$, $b=14.229(3)$, $c=23.401(4)$ \AA , $\beta=103.77(1)^\circ$. $[\text{HNEt}_3]_2[\text{VO}(\text{S}_2\text{C}_6\text{H}_4)_2]$ (1b) monoclinic, $P2_1/c$, $Z=4$, $a=8.236(1)$, $b=25.560(3)$, $c=13.637(3)$ \AA , $\beta=98.16(1)^\circ$, and $[\text{NEt}_4]_2[\text{VO}(\text{S}_2\text{C}_6\text{H}_4)_2]$ (1c) monoclinic, $P2/n$, $Z=4$, $a=18.540(3)$, $b=9.141(3)$, $c=18.970(4)$ \AA , $\beta=93.21(2)^\circ$. Vanadyl complexes (1) are useful precursors to the homoleptic complex $[\text{NEt}_4]_2[\text{V}(\text{S}_2\text{C}_6\text{H}_4)_3]$ (2) {orthorhombic, $Pbca$, $Z=8$, $a=13.613(3)$, $b=18.448(5)$, $c=26.845(5)$ \AA }. The six coordinate environment of 2 is comparable to those of $[\text{HNEt}_3]_2[\text{Mn}(\text{S}_2\text{C}_6\text{H}_4)_3]$ (3) {tetragonal, $P4_12_12$, $Z=4$, $a=10.319(2)$, $c=32.190(8)$ \AA } and $[\text{Li}]_3[\text{Cr}(\text{S}_2\text{C}_6\text{H}_4)_3]$ (4) {orthorhombic, $Pbcn$, $Z=4$, $a=15.788(3)$, $b=22.046(4)$, $c=13.092(3)$ \AA }.



PS08.00.21 HYDROGEN ATOM LOCALIZATION IN LAWSONITE USING SINGLE CRYSTAL PMR DATA. Kozlova S.G., Gabuda S.P., Armbruster T.*, Libowitzky E.*, Institute of Inorganic Chemistry, Novosibirsk, Russia; * University of Bern, Bern, Switzerland

The phase transition at 273 K in lawsonite is characterised by the loss of the mirror plane $-m$ due to the rotation of water molecules and OH groups [Libowitzky, Armbruster, *Am. Miner.* 1995, 90]. This transition may be displacive or of order-disorder type. In the latter case the $Cmcm$ phase, stable above 273K, must be orientationally disordered (either dynamically or statically). Proton magnetic resonance (PMR) spectroscopy was applied for the characterisation of the $Cmcm$ hydrogen sublattice at 295K.

A lawsonite crystal, $2\times 2\times 4\text{mm}^3$ in size was oriented with respect to its morphology as well as by optical and X-ray methods. The PMR spectra were measured at 12 MHz. The spectra revealed a resolved fine structure, caused by the dipole-dipole interactions in multi-spin system $[\text{OH-H}_2\text{O-OH-OH-H}_2\text{O}]$. The mean square widths (M) of the spectra recorded parallel to the crystallographic axes are as follows: $M[100]=19.6$; $M[010]=11.7$; $M[001]=50.3\text{ G}^2$ (error is 5%). The analysis of the fine structure of spectra and of the M values provide evidence that the hydrogen sublattice of the $Cmcm$ lawsonite structure is disordered. In a structural sense this disorder can be interpreted as a time averaged dynamic disorder of the H_2O and OH groups oscillating between two equivalent sites similar to the ordered H positions of the $Pm\bar{c}n$ lawsonite structure. The corrected for libration motion H-H distance is $R(\text{H}_2\text{O})=1.52\text{\AA}$, and mean-square angle of H-H librations is 0.18 rad^2 . Libration motion leads to distortion of X-ray and neutron diffraction data [Busing, Levy, *Acta Cryst.* 1963, 17, 142]. Using obtained values we calculated the "uncorrected" H-H distance, which will be observed in diffraction study: $R(\text{H}_2\text{O})=1.38\text{\AA}$, that is in excellent agreement with X-ray value $1.34(4)\text{\AA}$.