1.54Å. C-316 INORGANIC AND MINERAL SPECTROSCOPY

Bismuth sesquisulfide has attracted wide interest as fuel cell materials. It is an excellent oxygen ion conductor in its high temperature phase. This high temperature fluoride 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 Bi₂O₂V₂O₇ 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 6Bi₂O₂V₂O₇ compound has a 3x3x3 superstructure derived from the fluoride 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 6Bi₂O₂V₂O₇ compound has a pseudo monoclinic structure. The lattice is represented using the fluoride cell as, a=3/2(1.1.2), b=3/2(1.1.0), c=5/2(1.5.2) and beta=107.13. The structure is comprised 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 (0.6Å) 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 tilting structure with 21 (111) layers was observed around the composition Bi₂O₂V₂O₇. A microscopic model is presented for this tilting structure, where vanadium atoms come to the nearest neighbor sites at every seven layer and share oxygen vacancies in common.

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, Armbuster, Am. Miner. 80, 901]. This transition may be displacive or of order-disorder type. In the latter case the Cmcm phase, stable above 273K, must be dimensionally ordered (either dynamically or statically). Proton magnetic resonance (PMR) spectroscopy was applied for the characterisation of the Cmcm hydrogen sublattice at 295K.

A lawsonite crystal, 2x2x4mm³ 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 [OH-H₂O-OH-H₂O]. The mean square widths (M) of the spectra recorded in parallel to the crystallographic axes are as follows: M[001]=19.6; M[010]=11.7; M[001]=50.3 G² (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 H₂O and OH groups oscillating between two equivalent sites similar to the ordered H positions of the Pnma lawsonite structure. The corrected for libration motion H distance is R(H₂O)=1.52Å, and mean-square angle of H-H librations is 0.18 rad². Libration motion leads to distortion of X-ray and neutron diffraction study [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(H₂O)=1.38Å, that is in excellent agreement with X-ray value 1.34(4)Å.