

08.6-2 STRUCTURE OF  $\text{CsP}_8\text{W}_8\text{O}_{40}$ : A NEW DIPHOSPHATE TUNGSTEN BRONZE WITH OCTAGONAL TUNNELS. By M. Goreaud, Ph. Labbé and B. Raveau, Laboratoire de Cristallographie, Chimie et Physique des Solides, L.A. 251, ISMRA-Université, 14032 Caen Cedex, France.

Crystals of a new bronze  $\text{CsP}_8\text{W}_8\text{O}_{40}$  have been synthesized. They crystallize in the orthorhombic system ( $a = 13.061(1)$ ,  $b = 12.319(1)$ ,  $c = 5.2960(5)$  Å, S.G. : Pcmn). The structure, solved by the heavy-atom method, was refined to  $R = 0.023$  and  $R_w = 0.026$  for 1645 observed reflections.

The framework of  $\text{CsP}_8\text{W}_8\text{O}_{40}$  is built up from corner-sharing  $\text{WO}_6$  octahedra and  $\text{P}_2\text{O}_7$  diphosphate groups, building large octagonal tunnels where  $\text{Cs}^+$  ions are statistically distributed in off-centred positions. This original structure shows numerous relationships with those of other mixed valence tungsten phosphate bronze we have previously described, particularly with  $\text{P}_8\text{W}_{12}\text{O}_{52}$ . Structural slices of  $\text{CsP}_8\text{W}_8\text{O}_{40}$  are also compared with those of  $\text{K}_x\text{P}_2\text{W}_4\text{O}_{16}$ ,  $m = 4$  member of the monophosphate tungsten bronze series  $\text{A}_x(\text{PO}_2)_4(\text{WO}_3)_{2m}$  and  $\text{Rb}_2\text{P}_8\text{W}_{16}\text{O}_{64}$ ,  $m = 4$  member of the diphosphate tungsten bronze series  $\text{A}_x(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$ .

In the phosphate tungsten bronze family,  $\text{CsP}_8\text{W}_8\text{O}_{40}$ , which exhibits  $2 \times 2$   $\text{WO}_6$  octahedra wide  $\text{ReO}_3$ -type columns extending indefinitely along  $[001]$ , appears as the first potential unidimensional conductor.

08.6-3 ELECTRON AND SPIN ORDERING AND ASSOCIATED PHASE TRANSITIONS IN ILVAITE, A MIXED VALENCE IRON SILICATE. By SUBRATA GHOSE (Department of Geological Sciences, University of Washington, Seattle, WA 98195); A.W. HEWAT (Institute Max von Laue-Paul Langevin, 38042 Grenoble Cedex, France); M. MAREZIO (Laboratoire de Cristallographie, CNRS, 38042 Grenoble Cedex, France); N.V. DANG (LEPES, CNRS, 38042 Grenoble Cedex, France); R.A. ROBIE and H.T. EVANS (U.S. Geological Survey, 959 National Center, Reston VA 22092)

Ilvaite,  $\text{Ca}(\text{Fe}^{2+}, \text{Fe}^{3+})\text{Fe}^{2+}\text{Si}_2\text{O}_7\text{O}(\text{OH})$  contains double chains of Fe-octahedra (A sites) parallel to the  $c$  axis; half as many larger  $\text{Fe}^{2+}$  octahedra (B sites) are attached along the chains. The symmetry is orthorhombic (space group  $Pbmm$ ) at high temperature and monoclinic (space group  $P2_1/a$ ) at room temperature. A thermally activated  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  electron transfer occurs in the A sites above 400K (Heilmann et al. 1977, and others). Through high temperature x-ray diffraction, we have located the monoclinic to orthorhombic phase transition at 333-343K. Magnetic susceptibility measurements of ilvaite single crystals from Seriphos, Greece indicate a sharp paramagnetic to antiferromagnetic transition at 116K and another at 40K. Low temperature specific heat measurements also indicate two transitions at 120 and 40K. Rietveld profile analyses of high resolution neutron powder diffraction data at 300, 150, 80 and 5K indicate electron ordering at 300 and 150K resulting in distinct  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions within the monoclinic symmetry, confirming earlier x-ray results. At 80K the spins on the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in the A sites are ordered, while those on the  $\text{Fe}^{2+}$  ions in the B sites are disordered. At 5K, the spins on the  $\text{Fe}^{2+}$  ions on the B sites are ordered as well. Spins on both sites are parallel and antiparallel to the  $b$  axis.