

07.7-2 A STUDY OF SEMICONDUCTOR INTERCALATION IN ZEOLITE-Y USING POWDER SYNCHROTRON X-RAY DIFFRACTION. By M.M. Eddy, G.D. Stucky, J.E. MacDougall, Dept. of Chemistry, U.C.S.B., Santa Barbara, CA 93106, D.E. Cox, Department of Physics, Brookhaven National Lab., Upton, Long Island, New York 11973, and N. Herron, Experimental Station, E.I. du Pont de Nemours and Co., Wilmington, DE 19898.

High resolution x-ray powder diffraction data were collected for a series of CdS and CdSe intercalates in a host zeolite-Y framework. The measurements were made on beam line X13a at the National Synchrotron Light Source, Brookhaven National Laboratory. Each diffractogram was analysed using the profile fitting technique originally devised by Rietveld (H.M. Rietveld, J. Appl. Cryst., (1969), 2, 65), and the extra-framework material was located using standard Fourier methods. Four samples, with different concentrations of Cd, S and Se, were investigated and an example of the excellent agreement between observed (solid line) and calculated (dotted line) profiles for CdSe in zeolite-Y is given in Fig. 1. Also shown is the difference between these two curves.

In all cases Cd prefers to occupy a site within the sodalite unit, capping the double-6-ring, coordinated to three framework oxygens. Also associated with this particular Cd is an oxygen of a hydroxyl group or water molecule which results from inadequate dehydration and gives an octahedral arrangement around the cation. As the concentration of Cd is increased occupation of the 12-ring occurs. These results provide a possible explanation for the interesting results found from U.V. spectroscopy, which show that above a critical loading the intercalate acts like a semiconductor. Within the sodalite unit of zeolite-Y there exist cubes of cadmium and sulphur. These are discrete entities at low semiconductor loadings. However as the concentration is increased a network is set up which is modulated by the host framework.

* Work supported by the Division of Material Sciences, U.S. Dept. of Energy, under contract DE-AC02-76CH00016.

07.7-3 NEW CRYSTAL CHEMISTRY, NON-STOICHIOMETRIC AND GLASSY COMPOUNDS IN THE As-V-O SYSTEM.

J. Galv, R. Enjalbert, J.M. Savariault and A. Medouar, Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 TOULOUSE Cédex, France.

A thorough investigation of the As-V-O system allowed to synthesize new compounds or new polymorphs containing $As^{5+}V^{5+}$, $As^{5+}V^{4+}$ or mixed valences of vanadium $As^{5+}V^{5+}V^{4+}$. Crystal structures of the double oxides β -AsVO₅, AsV₃O₉ and As₂V₄O₁₃ were determined giving a new insight in the general chemical system As-V-O and its potentialities in the field of intercalation chemistry, catalysis and conduction properties of alkaline doped glassy families $As_2^{5+}V_{2x}^{5+}V_{4-4x}^{4+}O_{13+x}$ and $As_2^{5+}As_{2y}^{3+}V_{4-4y}^{4+}O_{13+3y}$ (with $x \leq 1$ and $y \leq 1$).

β -AsVO₅ crystallizes in the monoclinic system, space group P2₁/n. The crystal structure is rather different from α -AsVO₅ previously structurally investigated by N. G. Chernorukov et al. (Russian J. of Inorg. Chem., 1978, 23, 10, 1475-1481) and its intercalation potentialities reported by J. W. Johnson et al. (Inorg. Chem., 1982, 21, 3820-3825). β -AsVO₅ is a layer structure built up from square pyramids VO₅ associated in pairs by edge sharing, these blocks being corner shared to AsO₄ tetrahedra.

AsV₃O₉, orthorhombic system, space group Pbca, contains infinite double strings of octahedra (V₂O₈)_n sharing edges and corners, running parallel to [100] and via interconnected (As₂O₇) groups. Structurally, this compound localized on the pseudo-system As₂V₂O₉-V₄O₉, shows similarities with β -AsVO₅.

As₂V₄O₁₃ is triclinic, exhibiting a rather complex cation distribution in a cubic close packed array of oxygen atoms (R. E. Enjalbert et al., Acta Cryst., 1986, C 42, 1465-1467).

Structural investigation of the amorphous compounds mentioned above has been performed using both LAXS and EXAFS techniques.

On the base of these structural informations intercalation chemistry has been developed using organic molecules or metal complexes. The aim of this contribution is to discuss these subsequent results which are directly related too with the P-V-O system widely explored (E. Bordes et al., J. Chem. Soc. Chem. Comm., 1985, 294-296, ...).

