14.4-9   A STUDY OF CATION ORDERING IN SPINELS BY CONVERGENT BEAM ELECTRON DIFFRACTION AND IMAGING   By A.F.Moodie and H J Whitfield , Division of Materials Science and Technology, CSIRO, Locked Bag 33, Clayton, Victoria, Australia, 3168

The cubic spinel has general structural formula $A[B_2]X_4$ and protoype symmetry Fd3m. Spinel structures containing more than one kind of metal atom can arrange themselves in ordered superlattices. The strength of superstructure reflections is correlated with the difference in scattering power between the ordered ions. Convergent beam electron diffraction can be used to detect superlattice reflections below the limits of detection by X-rays. Furthermore symmetry associated information such as the existence of extinction bands may be obtained from quite small crystals. Convergent beam electron diffraction and lattice imaging of microcrystals of the oxides $Li_2ZnTi_3O_8$, $Zn_2Ti_3O_8$, $LiMn_2O_4$ and Mn_3O_4 were obtained and give information on the degree of order, faulting and microstructures not observable from the powder X-ray diffractograms. Thus CBED of the spinel $Li_2ZnTi_3O_8$ shows extinction bands that confirm its space group is $P4_332$ in accord with a spinel superstructure of 1:3 ordering of Li and 3Ti on octahedral B sites and random distribution of Li and Zn on tetrahedral A sites.

Solid state reaction of $Li_2ZnTi_3O_8$ with $ZnSO_4$ gives replacement of pairs of Li atoms by a Zn atom plus a cation vacancy. Extinction bands in the CBED of the product shows that there is 1:3 ordering of vacancies and Ti atoms on octahedral sites.

Mn_3O_4. a tetragonally distorted spinel of space group $I4_1/amd$ that occurs naturally as the mineral hasumannite, was prepared by thermal decomposition of $MnCO_3$ in air at 750 to 800°C. It is stable in the electron beam of the JEOL 200 C microscope and gives good CBED and lattice images. Typical macroscopic samples that show rather broad diffuse X-ray powder diffraction lines are found on examination with electrons to consist of a mixture of well-crystallized perfect regions of crystal and highly faulted regions of crystals. Decomposition of $MnCO_3$ at somewhat lower temperatures produces a mixture of Mn_3O_4 and Mn_2O_3. CBED and lattice images give information of the topographical relation of these oxides.

14.4-10   CRYSTAL STRUCTURE DETERMINATION OF BLATTERITE USING ANALYTICAL ELECTRON MICROSCOPY By A. Olsen [1] and G. Raade [2], 1) Institute of Physics, University of Oslo, P.O. Box 1048, 0316 Oslo 3, Norway, 2) Mineralogical-Geological Museum, University of Oslo, N-0562 Oslo 5, Norway.

Blatterite is a new oxyborate mineral from Nordmark, Sweden, recently approved by the I.M.A. Commission on New Minerals and Mineral Names. A detailed description of occurrence, optical properties, chemical composition of bulk specimens and X-ray diffraction data will be published elsewhere (Raade et al., in preparation).

The present paper reports a structure determination of blatterite by a combination of HREM, CBED and X-ray microanalysis. SAD patterns were used to determine approximate cell dimensions. Blatterite was found to be orthorhombic with space group Pnnm or Pnn2. Least squares refinements of X-ray powder data gave the following cell dimensions of bulk specimens:
a = 37.693(6), b = 12.620(2), c = 6.2541(8) Å. HREM of [001] projections revealed a zig-zag type contrast characteristic of a twinned type structure. Blatterite was found to be related to the other members of the pinakiolite group, but the mineral was found to have a 8t8t.. type structure which has not been observed before among the other members. Although HREM studies demonstrated rather large areas of crystals with the same structure type, variations in the periodicity along the a axis were also observed.

Chemical analysis of bulk specimens corresponds to $(Mn^{2+}_{1.21}Mg_{0.79})(Mn^{3+}_{0.69}Sb^{3+}_{0.19}Fe^{3+}_{0.11})(B_{1.01}O_3)O_2$, but X-ray microanalysis also demonstrated variations in the composition. In order to investigate the local symmetry CBED patterns were explored.

14.4-11   IMAGE SIMULATIONS AND IMAGE PROCESSING OF HREM IMAGES OF METAL-LOADED ZEOLITES.   By H.W. Zandbergen, Gorlaeus Laboratory, State University Leiden, P.O. Box 9502, 2300 RA Leiden, Netherlands; and W. Coene and D. van Dyck, University of Antwerp RUCA, Groenenborgerlaan 171, B-2020 Antwerp, Belgium.

Metal loaded zeolites are of industrial interest because they can catalyse a number of reactions shape-selectively. This selectivity arises from the pores of the zeolites. Because the size of the pores depends on the type of zeolite, shape selectivity can be tuned to the reaction products desired.

For two reasons high resolution electron microscopy (HREM) is carried out on metal loaded zeolites. In the first place to determine the metal particle size distribution. In this case the best procedure is to destroy the zeolite lattice by the electron beam (Zandbergen et al, Appl. Catal. 25, 231 1986). Because of the beam sensitivity this can be done very easily.

The second reason to perform electron microscopy is to determine the positions of the metal particles inside the zeolite lattice. Because the image recorded depends on a number of experimental conditions, the positions of the metal particles in the zeolite matrix cannot be determined without doing image simulations for the zeolite lattice. Using image simulations (D. Van Dyck and W. Coene, Ultramicroscopy 15, 29 (1984)) at several values of defocus and crystal thickness the positions of the pores can be pinpointed.

For the determination of the size, location and shape of the metal particles, image processing can be of great help. For instance the shapes of the metal particles can be made better visible, by extraction all periodic information in Fourier space or by substracting an averaged image from the original one. On the other hand a better image of the zeolite lattice itself can be obtained by extraction of all non periodic information. Using Stereo HREM the 3d positions of the metal particles can be determined.