

14.4-6 ON THE STRUCTURE OF  $\text{Pr}_{24}\text{O}_{44}$ : A STUDY BY HIGH RESOLUTION ELECTRON MICROSCOPY. By E. Schweda, D.J. Smith and L. Eyring, Department of Chemistry and Center for Solid State Science, Arizona State University, Tempe, AZ 85287, U.S.A.

The end member observed in the homologous series ( $\text{Pr}_n\text{O}_{2n-2}$ ) of intermediate praseodymium oxides is  $\text{Pr}_{12}\text{O}_{22}$  (L. Eyring, P. Kunzmann, J. Solid State Chem. 14 (1975) 229). The unit cell is determined from electron diffraction patterns. The images used for determination of the defect positions are taken along the  $[21\bar{1}]$  axis of the fluorite substructure. The model developed for matching the micrographs taken on a JEOL 4000EX were based on a defect cluster that is known as "Bevan Cluster" (D.J.M. Bevan et al., Acta Cryst. B24 (1968) 1183. The distorted cluster represents the structure of  $\text{Pr}_7\text{O}_{12}$ . If the structure of  $\text{Pr}_7\text{O}_{12}$  can be considered to be the prototype structure of all the other intermediate oxides ( $\text{Pr}_2\text{O}_3$  -  $\text{PrO}_2$ ) then all these phases are built by these kinds of isolated defects arranged in different ways for different phases.

$\text{Pr}_7\text{O}_{12}$  appears to be the closest packing of these defect clusters in the space group  $R\bar{3}$  (IT: #148). Every other arrangement decreases the point group symmetry to  $P\bar{1}$  and finally to  $P1$ . Those space groups are related by a direct group-subgroup relationship. Four models with distorted and undistorted anion sublattices are compared. The Pendellösung plots for the 15 strongest fluorite reflections and the overall intensity for the superstructure reflections have been calculated. They show that at a crystal thickness of 140 Å the intensity is chiefly based on the superstructure reflections. The images taken at that crystal thickness will depend on the distortions of oxygen. The calculated images of these four models are compared with a through-focus series of images from a wedge-shaped crystal in order to match the contrast.

14.4-7 ELECTRON BEAM INDUCED MODIFICATIONS IN POTASSIUM  $\beta''$ -FERRITE ( $\text{K}_2\text{O} \cdot 4\text{FeO} \cdot 15\text{Fe}_2\text{O}_3$ ).

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Potassium  $\beta''$ -ferrite,  $\text{KFe}_{17}\text{O}_{25}$ , a sodium  $\beta''$ -alumina isotype, with a hexagonal structure consisting of slabs of spinel separated by loosely packed conduction planes (Matsui *et al.*, Acta Cryst. 1985, B41, 27-32), has been studied by 400 kV High Resolution Transmission Electron Microscopy at 1.5 Å resolution. HRTEM images, with the incident electron beam normal to the (110) and (100) planes of oriented crystals, show all the projected cation sites clearly in undamaged crystals.

This presentation will describe the various stages of structural damage which accompany prolonged electron irradiation:

- (1) Migration of  $\text{K}^+$  and  $\text{O}^{2-}$  ions from conduction planes,
- (2) Frequent collapse of conduction planes,
- (3) Topotactic transformation of the multiply-twinned spinel layers to form broad laths of magnetite,  $\text{Fe}_3\text{O}_4$ ,
- (4) Gradual growth of wüstite,  $\text{Fe}_{1-x}\text{O}$  on exposed  $\text{Fe}_3\text{O}_4$  surfaces.

Selected area electron diffraction patterns confirm these structural changes. Possible mechanisms for these transformations will be discussed.

14.4-8 STRUCTURAL STUDIES TO ATOMIC RESOLUTION OF INORGANIC CRYSTALS AND QUASICRYSTALS BY ELECTRON MICROSCOPY AND CRYSTALLOGRAPHIC IMAGE PROCESSING. Da Neng Wang and Sven Hovmöller, Structural Chemistry, University of Stockholm, S-106 91 Stockholm, Sweden.

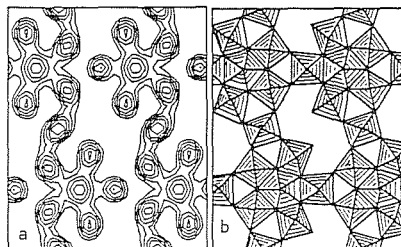
Electron microscopy has become an alternative to X-ray diffraction as a method for structure determination. The advantage of EM over X-rays is mainly that the phases are not lost, since the diffracted electrons are focussed into an image. The stronger interaction of electrons with matter, compared to that of X-rays, makes it possible to study much smaller crystals. Indeed even aperiodic features can be studied by EM. The resolution is about 2Å.

The limitations of EM are mainly two; the narrow range of validity of kinematical scattering and optical distortions by the lenses of the microscope. For thin crystals (<40Å for inorganic crystals) dynamical effects may be neglected. The optical distortions are mainly caused by only 5 variables; the defocus value (1), the stigmatism (2) and the beam tilt (2 variables). In addition crystal tilt, defined by 2 variables, affects the image. If all these 7 variables can be determined and corrected for a distortion-free image can be obtained at atomic resolution.

We have obtained such distortion-free images of crystalline metal oxides by a procedure which we call crystallographic image processing (CIP). The EM image is digitized by a microdensitometer, and its Fourier transform (FT) is calculated by computer. The FT contains both amplitude AND PHASE information, although both amplitudes and phases are more or less distorted by the optics. When the crystal has some symmetry, crystallographic constraints will be put on the amplitudes and/or phase values. The distortions in the image will show up as violations of the crystallographic constraints. Since different distortions have different effects on phases and amplitudes it is possible to determine and correct for the distortions in the electron micrograph. The corrected amplitudes and phases are then used as input to a conventional FT program which calculates a density map.

The crystalline structures of  $\text{K}_7\text{Nb}_{15}\text{W}_{13}\text{O}_{80}$  (Hovmöller et al. Nature 311 (1984) 238-241),  $\text{Na}_6\text{Nb}_{24}\text{O}_{62}\text{F}_2$  and a compound of unknown composition in the system Cs-Nb-O-F were determined by EM and CIP. The results were compared to the structures of isomorphous compounds studied by X-ray diffraction. The average deviation of atomic positions for the heavy metal atoms between EM and X-ray was only 0.10Å. Oxygen atoms were not resolved at this resolution.

Similar image processing has also been applied to EM images of quasicrystals as a means to study the modulations of the structural theme. For  $\text{Al}_{13}\text{Mn}$  quasicrystals both the positions and the amplitudes and phases of the diffraction points change from one area of the image to another adjacent area.



Structure of  $\text{K}_7\text{Nb}_{15}\text{W}_{13}\text{O}_{80}$  determined by a) EM-CIP b) X-ray.