

Twenty-seven-layer barium chromium oxide, BaCrO_3 , was prepared at 1200°C and 60–65 kbar by reaction of CrO_2 and Ba_2CrO_4 . The compound crystallizes in space group $R\bar{3}m$ with hexagonal cell dimensions $a = 5.652 \pm 0.002 \text{ \AA}$, $c = 62.75 \pm 0.02 \text{ \AA}$. The structure was determined from 1070 independent reflections, of which 811 were considered observed, collected by automated counter methods and refined by least-squares methods to a conventional R value of 4.1%. The structure consists of a 27-layer stacking sequence of close-packed BaO_3 layers, Zhdanov notation for the sequence (3)2(2)2, with all of the O_6 octahedral sites occupied by Cr. Strings of four pairs of face-sharing octahedra in which the pairs are linked to each other by corner sharing are in turn joined to each other by octahedra sharing only corners. The structure is thus closely related to the four-layer and six-layer polytypes of BaCrO_3 . Bariums in two of the five crystallographic positions showed large thermal anisotropy and are better described in terms of half-atom occupancy in split sites.

Neutron Diffraction Experiments on CsCrI_3 at 300, 77, and 1.2°K. H. W. ZANDBERGEN AND D. J. W. IJDO. Gorlaeus Laboratories, University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands. CsCrI_3 has been investigated by neutron powder diffraction at room temperature, 77°K, and 1.2°K. It undergoes a phase transition at 150°K due to the cooperative Jahn–Teller effect. The high-temperature form, $\alpha\text{-CsCrI}_3$ (hexagonal, space group $P6_3/mmc$, $a = 8.127(1) \text{ \AA}$, $c = 6.944(1) \text{ \AA}$, $Z = 2$), adopts the BaNiO_3 structure with a local Jahn–Teller distortion. The low-temperature form $\beta\text{-CsCrI}_3$ (orthorhombic, space group $Pbcn$, $a = 8.102(1) \text{ \AA}$, $b = 13.792(1) \text{ \AA}$, $c = 6.900(1) \text{ \AA}$, $Z = 4$), has a structure not yet reported for a Jahn–Teller distorted BaNiO_3 structure. It is shown that the low-temperature form can be derived from the BaNiO_3 structure by means of canting of triangles, formed by the three common I^- ions of two adjacent CrI_6^{4-} octahedra. The magnetic structure of $\beta\text{-CsCrI}_3$ at 1.2°K is found to consist of an antiparallel sequence of ferromagnetic (001) planes with a magnetic moment in the $|100|$ direction of $3.26 \mu_B$.

X-Ray Study of the Ordering of the Alkali Ions in the Intercalation Compounds Na_xTiS_2 and Li_xTiS_2 . TJPKE HIBMA. Brown Boveri Research Center, CH-5405 Baden-Dättwil, Switzerland.

The arrangement of the alkali ions in electrochemically intercalated TiS_2 crystals was studied by diffuse X-ray techniques. In Na_xTiS_2 a stage 3 phase was discovered in addition to the known stage 1 and 2 phases. Three types of three-dimensionally ordered superstructures were observed: a $(3^{1/2} \times 3^{1/2})$ superstructure for stage 2 and 3 phases, a (2×2) and a $(2 \times 3^{1/2})$ superstructure for stage 1 and 2 phases. The appearance of these superstructures is consistent with a screened Coulomb interaction between the sodium ions. In the single-phase region above $x = \frac{1}{2}$, diffuse rings show up in addition to the $(2 \times 3^{1/2})$ superlattice. These rings are caused by local rearrangements of the ions to accommodate the excess sodium ions. The $(3^{1/2} \times 3^{1/2})$ and (2×2) superstructures were also observed in Li_xTiS_2 crystals.

Studies of Layered Uranium(VI) Compounds. III. Structural Investigations of Hydrogen Uranyl Phosphate and Arsenate Tetrahydrates below the Respective Transition Temperatures of 274 and 301°K. MARK G. SHILTON AND ARTHUR T. HOWE. Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, England.

The layered hydrates $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ (HUP), and $\text{HUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ (HUAs), which are proton-conducting solid electrolytes above the conductivity transitions at 274 and 301°K respectively, have been shown, using powder X-ray diffraction, to change from tetragonal to orthorhombic symmetry below these temperatures. For HUP the unit-cell dimensions were $a = 6.985(5)$ and $c = 17.45(1) \text{ \AA}$ at 290°K, and $a = 6.966(5)$, $b = 7.004(5)$, and $c = 17.43(1) \text{ \AA}$ at 260°K. The values for HUAs were $a = 7.150(2)$ and $c = 17.608(5) \text{ \AA}$ at 305°K, and $a = 7.128(2)$, $b = 7.168(2)$, and $c = 17.613(5) \text{ \AA}$ at 293°K. The enthalpies of these displacive-type transitions were found from differential scanning calorimetry to be less than 0.5 kJ per mole of water for both compounds. Such a small value indicates that the rigid-like water lattices existing below the transitions do not become liquid-like above the transitions. The infrared spectra of HUP and HUAs both above the transitions and down to 80°K showed clear evidence of the presence of H_3O^+ ions, showing that the conductivity transitions are not caused by a loss of carriers. Rather, the antiferroelectric ordering, known to exist for HUAs, would appear to cause the conductivity drop. Upon this indication of ordering within the water layers, two possible related H-bond ordered structures have

been proposed which are consistent with the observed twinning behavior and cell symmetry. The same ordered structures are suggested for HUP from our observations of the twinning behavior.

Studies of Layered Uranium (VI) Compounds. IV. Proton Conductivity in Single-Crystal Hydrogen Uranyl Phosphate Tetrahydrate (HUP) and in Polycrystalline Hydrogen Uranyl Arsenate Tetrahydrate (HUAs). ARTHUR T. HOWE AND MARK G. SHILTON. Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, England.

Single-crystal measurements on hydrogen uranyl phosphate tetrahydrate, $\text{H}_2\text{UO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ (HUP), have confirmed that the high proton conductivity is a bulk characteristic. The conductivity values were in substantial agreement with those previously reported for polycrystalline disks. A conductivity of $0.6 \text{ ohm}^{-1} \text{ m}^{-1}$ at 290°K and an activation energy of $30 \pm 1 \text{ kJ mole}^{-1}$ were measured parallel to the structural layers of the crystal. The conductivity was at least 100 times lower when measured in the perpendicular direction. A reasonable attempt frequency ω_0 of approximately 10^{15} Hz could be derived from the parallel conductivity on the assumption that the charge carrier concentration was equal to that of the H_3O^+ ions. This implies a low proton mobility, of the order of $10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ sec}^{-1}$ at 290°K , in support of previous estimates. We have also shown that polycrystalline hydrogen uranyl tetrahydrate, $\text{H}_2\text{UO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ (HUAs), has a high conductivity of $0.6 \text{ ohm}^{-1} \text{ m}^{-1}$ at 310°K , with an activation energy of $31 \pm 2 \text{ kJ mole}^{-1}$. Below the respective dielectric ordering transition temperatures of HUP and HUAs of 274 and 301°K , the lower conductivity values show a marked frequency dependence, which may be due to dispersion effects caused by water reorientations.

Topotaxial Decomposition of Calcite-Type KNO_3 Crystals. S. W. KENNEDY AND W. M. KRIVEN. Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, S.A. 5001, Australia.

The calcite-like form of potassium nitrate, KNO_3 , decomposed under the transmission electron microscope to form KNO_2 which subsequently decomposed giving the high-temperature β form of K_2O . Two closely related orientation relations were observed for KNO_2 . Referred to the four molecule cell of KNO_3 , they were $[111]_{\text{KNO}_3} \parallel [111]_{\text{KNO}_2}$, $(0\bar{1}1)_{\text{KNO}_3} \parallel (0\bar{1}1)_{\text{KNO}_2}$; and $[100]_{\text{KNO}_3} \parallel [100]_{\text{KNO}_2}$, $(001)_{\text{KNO}_3} \parallel (001)_{\text{KNO}_2}$. These and a different published orientation relation for the decomposition of cadmium carbonate conform, respectively, to orientations resulting from a corresponding structural phase transformation in rubidium nitrate. $\beta\text{-K}_2\text{O}$ formed with its cube axes parallel to those of KNO_2 . Both nitrate and carbonate reactions can be regarded as topotaxial. Application of the crystallographic approach to orientations and accommodation of misregistry is discussed.

Structure Cristalline de la Phase $\beta\text{-KEr}_2\text{F}_7$ Composés Isotypes. S. ALEONARD, Y. LE FUR, M. F. GORIUS ET M. TH. ROUX. Laboratoire de Cristallographie, CNRS 166X-38042 Grenoble Cedex, France.

Potassium erbium fluoride $\beta\text{-KEr}_2\text{F}_7$ crystallizes in the orthorhombic system, space group $Pna2_1$, with the unit-cell dimensions $a = 11.820 \text{ \AA}$, $b = 13.333 \text{ \AA}$, $c = 7.816 \text{ \AA}$ ($Z = 8$). The crystal structure has been solved from single-crystal diffractometer measurements ($\text{AgK}\alpha$) by Patterson and Fourier synthesis and refined by a least-squares method. The final R value is 0.042 for 2374 independent observed reflections ($R_w = 0.051$). The four species of erbium atoms are surrounded by eight fluorine atoms. These fluorine atoms form, respectively, three quadratic antiprisms and one dodecahedron, derived from a distorted cube. Two antiprisms and the dodecahedron share two of their faces to form $(\text{Er}_3\text{F}_{17})^{8-}$ groups. These groups are bidimensionally linked and the planes they form are joined together by the third antiprism. A three-dimensional network is then produced, in the tunnels of which potassium atoms are located. Lattice parameters of compounds which are isotypes to the new structure type of $\beta\text{-KEr}_2\text{F}_7$ are given.

Thermodynamische Untersuchungen am System CoO/MgO . K. TORKER UND W. INSELSBACHER. Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, A-8010, Austria.

A series of solid solutions, $\text{Co}_x\text{Mg}_{1-x}\text{O}$, was studied thermodynamically in the range $1100\text{--}1300 \text{ K}$ by means of solid state galvanic cells using oxygen-ion conductors. The activities of CoO in the solid solutions show positive deviations from Raoult's law. The solid solutions are interpreted to be regular within the