

Abstracts of Forthcoming Articles

Ultramicrostructural Characteristics of Some Intercalates of Graphite: An Electron Microscopic Study. E. L. EVANS AND J. M. THOMAS. Edward Davies Chemical Laboratories, The University College of Wales, Aberystwyth, SY23 1NE, United Kingdom. The ultramicrostructure of certain graphite-intercalate residue compounds known to exhibit ordering has been investigated using high-resolution transmission electron microscopy and electron diffraction. Some novel ternary graphite-intercalates formed as a result of interactions between existing intercalates and other guest species have also been investigated. The superlattice patterns associated with the ordering of the intercalating species are readily interpretable, and it has been possible to obtain direct lattice images of the $\{10\bar{1}0\}$ graphite (0.21 nm) of the $\{100\}$ intercalated FeCl_3 (0.52 nm) and of $\{10\bar{1}0\}$ intercalated potassium (0.36 nm). It is shown that potassium acts as an effective reducing agent and, in the graphite-ferric chloride-potassium system, free iron and potassium chloride are formed. The catalytic activity of this ternary intercalate is probably associated with highly dispersed free iron.

The Structure of Defect Ru_4Si_3 . S. ANDERSSON, C. LEYGRAF, T. JOHNSON. Inorganic Chemistry II, Chemical Centre, Lund, Sweden. The nature of the defect structure of Ru_4Si_3 has been studied with electron diffraction and electron microscopy methods. Lattice image pictures, interpreted with histogram analysis, reveal that planar defects of chemical twinning type are common in the crystals.

Oxydes de Plomb. II. Etude Structurale à 5 K de la Phase Orthorhombique de l'Oxyde Pb_3O_4 . J. R. GAVARRI, G. CALVARIN, AND D. WEIGEL. Laboratoire de Chimie, C.S.P. Université Paris, Nord et Ecole Centrale des Arts et Manufactures, 92290 Chatenay-Malabry, France. The structure of Pb_3O_4 at 5 K has been studied from X-ray and neutron diffraction patterns. The cell is orthorhombic: $a = 9.124 \text{ \AA}$, $b = 8.467 \text{ \AA}$, and $c = 6.566 \text{ \AA}$. Twelve coordinates of lead and oxygen atoms have been refined from space group $Pbam$. From neutron diffraction data, an R value of 0.030 has been obtained, while the R value from X-ray diffraction data is 0.06. The interatomic $\text{Pb}^{\text{IV}}\text{-O}$ and $\text{Pb}^{\text{II}}\text{-O}$ distances are compared with those found in the quadratic structure: the $\text{Pb}^{\text{II}}\text{-O}$ bonds are longer than those found at 293 K.

Préparation et Structure d'un Polyphosphure de Magnésium: MgP_4 . A. E. MASLOUT, M. ZANNE, J. JEANNOT, AND C. GLEITZER. Laboratoire de Chimie du Solide, C.N.R.S. No. 158, Service de Chimie Minérale A, No. 140, 54037 Nancy Cedex, France. This compound is prepared through reaction of gaseous phosphorus with Mg_3P_2 at 600°C in a sealed silica tube. Evidence for a primitive monoclinic cell is obtained from electron microdiffraction; a refinement from X-ray powder diagrams provide the atomic positions; the compound is isotypic with CdP_4 .

Etude de la Tétracoordination de l'Étain dans deux Orthothioestannates: Na_4SnS_4 et Ba_2SnS_4 (α). J. C. JUMAS, E. PHILIPPOT, F. VERMOT-GAUD-DANIEL, M. RIBES, AND M. MAURIN. Laboratoire de Chimie Minérale C, E.R.A. 314, Université des Sciences et Techniques du Languedoc, Place Eugene Bataillon, 34060 Montpellier Cedex, France. The crystal structure of Na_4SnS_4 and Ba_2SnS_4 (α) were determined. Na_4SnS_4 crystallizes in tetragonal system, space group $P4_2$, c with parameters $a = 7.837 \text{ \AA}$, $c = 6.950 \text{ \AA}$, $Z = 2$, and Ba_2SnS_4 (α) in the monoclinic system, space group $P2_1/c$ with $a = 8.481 \text{ \AA}$, $b = 8.526 \text{ \AA}$, $c = 12.280 \text{ \AA}$, $\beta = 112.97^\circ$ and $Z = 4$. In these compounds, the crystal structure is built up from discrete orthothioestannate tetrahedra SnS_4 . The structure of Ba_2SnS_4 (α) is modified K_2SO_4 type.

Etude Thermodynamique des Oxydes TiO_{2-x} à 1050°C . C. PICARD AND P. GERDANIAN. Laboratoire des Composés Nonstoechiométrique, Université de Paris—Sud, Centre d'Orsay, 91405 Orsay, France. $g_{\text{O}_2}^{\text{M}}$ (O/Ti) and $h_{\text{O}_2}^{\text{M}}$ (O/Ti) have been directly measured at 1050°C within the whole homogeneity range

of the rutile phase TiO_{2-x} , respectively, using the method of equilibrium between oxides and buffer gaseous mixtures and by means of a high temperature microcalorimeter. These results are discussed in terms of point defects.

The Iodates of Scandium. K. NASSAU AND J. W. SHIEVER. Bell Laboratories, Murray Hill, New Jersey 07974. A dihydrate, a monohydrate, and three polymorphs of the anhydride $\text{Sc}(\text{IO}_3)_3$ have been prepared and studied, $\text{Sc}(\text{IO}_3)_3 \cdot 2\text{H}_2\text{O}$ was prepared by gel growth and by precipitation and evaporation at room temperature. The γ -anhydride can be crystallized from boiling water or nitric acid solution. The other compounds are formed on heating the dihydrate, which also dehydrates very slowly at room temperature. The α -anhydride is amorphous. The β -anhydride generates second harmonics, with about twice the efficiency of quartz. In addition, DTA, TGA, infrared absorption, and powder X-ray diffraction results are presented.

High Resolution Electron Microscopy of Crystallographic Shear Structures in Tungsten Oxides. S. IJIMA. Department of Physics, Arizona State University, Tempe, Arizona 85281. A crystallographic shear (CS) structure in reduced crystals of WO_3 has been imaged at a resolution of 3–4 Å by a high resolution electron microscope. A large distortion of the WO_6 octahedra sharing their edges at the CS planes has been directly recognized in the electronmicrographs. The CS occurs preferentially in a particular crystallographic orientation. The preference may be explained by a different degree of distortion along the principal axes in the WO_6 octahedra of the pseudocubic structure of WO_3 crystal. A model for growth and ordering of the CS planes is discussed.

Etude Structurale de $\text{Na}_4\text{Sn}_3\text{S}_8$ Evolution de la Coordination de l'Etain dans le Systeme $\text{Na}_2\text{S}-\text{SnS}_2$. J. C. JUMAS, E. PHILIPOTT, AND M. MAURIN. Laboratoire de Chimie Minerale C, ERA 314, Université des Sciences et Techniques du Languedoc, Place Eugene Bataillon, 34060 Montpellier Cedex, France. The crystal structure of $\text{Na}_4\text{Sn}_3\text{S}_8$ has been determined. This compound crystallizes in the monoclinic system space group $C2/c$ with the following parameters: $a = 11.427$, $b = 7.337$, $c = 17.621$ Å, $\beta = 95.27^\circ$, and $z = 4$. The structure has been solved with the help of a tridimensional Patterson synthesis. The reliability factor after refinement converges to 0.043 for 1620 independent reflexions. The structure contains SnS_4 tetrahedra and SnS_5 trigonal bipyramids linked together to form a tridimensional lattice of general formula $(\text{Sn}_3\text{S}_8)_n$.

Energy Transfer in Mercury-Doped Calcium Tungstate and Molybdate. G. BLASSE. Solid State Department, Physical Laboratory, University of Utrecht, Sorbonnelaan 4, Utrecht, The Netherlands. The luminescence of $\text{CaWO}_4\text{-Hg}$ and $\text{CaMoO}_4\text{-Hg}$ is reported. The presence of Hg^{2+} ions in the CaWO_4 lattice influences the luminescence of pure CaWO_4 drastically due to efficient energy transfer from host lattice groups to the emitting center consisting of a tungstate group with a neighboring mercuric ion. The luminescence characteristics of $\text{CaMoO}_4\text{-Hg}$ do not differ strongly from those of pure CaMoO_4 due to the absence of efficient energy transfer.

Electronic Conductivity in Nonstoichiometric Cerium Dioxide. R. N. BLUMENTHAL AND R. K. SHARMA. Metallurgy and Materials Science, College of Engineering, Marquette University, Milwaukee, Wisconsin 53233. The electrical conductivity of sintered specimens of nonstoichiometric CeO_{2-x} was measured as a function of temperature (750–1500°C) and oxygen pressure ($1-10^{-22}$ atm). The isothermal compositional dependence of the electrical conductivity of CeO_{2-x} was determined by combining recently obtained thermodynamic data, $x = x(P_{\text{O}_2}, T)$, with the conductivity data. The compositional and temperature dependence of the electrical conductivity may be represented by the expression

$$\sigma = 410[x]e^{-(0.158+x)/kT}(\text{ohm-cm})^{-1}$$

over the temperature range 750–1500°C and from $x = 0.001$ to $x = 0.1$. This expression was rationalized in terms of the following simple relations for (a) the electron carrier concentration $n_{\text{CeCe}'} = (8x)/a_0^3$ where $n_{\text{CeCe}'}$ is the number of CeCe' per cm^3 and a_0 is the lattice parameter and (b) the electron mobility

$$\mu = 5.2(10^{-2})e^{-(0.158+x)/kT}(\text{cm}^2/\text{V sec}).$$