Abstracts of Forthcoming Articles

Accommodation of Oxygen Loss in WO_3 Equilibrated With $CO + CO_2$ Buffers. SVEN BERGLUND AND WUBESHET SAHLE, Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden. Tungsten trioxide reduced at about 1270 K by means of controlled atmospheres ($P_{O_2} = 3.7 \cdot 10^{-8}$ to $1.7 \cdot 10^{-13}$ atm) was studied by high-resolution transmission electron microscopy, electron diffraction, and X-ray powder diffraction. The accommodation of oxygen loss in the parent WO_3 lattice in the range WO_3 to $WO_{2.72}$ was clarified. The results indicate a solid-state mechanism. Intergrowth has been found to take place between several of the structural types that occur in this composition range. The intergrowth features include directional changes in shear plane arrays ("swinging shear planes"). Details of the structural variation with the oxygen content are reported. Ordered shear planes on {102} directions were found to stabilize the orthorhombic WO_3 parent lattice at room temperature. $W_{24}O_{68}$ has been prepared in a fairly well-defined state.

Structure and Properties of the New Phase of the Pseudo-One-Dimensional Compound TaS_3. A. MEERSCHAUT, L. GEUMAS, AND J. ROUXEL, Laboratoire de Chimie des Solides, Université de Nantes, 2, rue de la Houssiniere, 44072 Nantes Cedex, France. The structure of a new form of tantalum trisulfide has been determined from single-crystal X-ray diffraction data and refined to an R value of 0.025. The unit cell is monoclinic with space group $P2_1/m$: $a = 9.515(2)$ Å, $b = 3.3412(4)$ Å, $c = 14.912(2)$ Å, $\beta = 109.99(2)°$. The structure consists of sulfur triangular prisms stacked on top of each other by sharing triangular faces. The tantalum atoms are located close to the center of the prisms which are parallel to the b twofold axis. The prisms are linked together in the c direction to form slabs parallel to the b–c plane. This arrangement is very like that observed in $NbSe_3$. The physical properties, especially the metal–semiconductor transition at 210 K, are discussed according to the structural features such as metal–metal distances and the existence of different S–S pairs.

High n-Value Phases in the Complex Bismuth Oxides with Layered Structure, $Bi_2CaNa_{n-2}Nb_nO_{3n+3}$. KUNITAKA MURAMATSU, MASAJI SHIMAZU, JUNZO TANAKA, AND SHIGEO HORIUCHI, National Institute for Research in Inorganic Materials, Sakuramura, Niihari-gun, Ibaraki 305, Japan. Complex bismuth oxides with layered structure are prepared with a series of compositions in the system $Bi_2CaNb_2O_9$–$NaNbO_3$. It is found by X-ray powder diffraction that each compound is composed of more than two phases, which are described by the formula $Bi_2CaNa_{n-2}Nb_nO_{3n+3}$; e.g., in the sample with the nominal composition $Bi_2CaNb_2O_9 \cdot 8NaNbO_3$; the phases with $n = 6$ to 8 appear predominantly. These phases are closely intergrown with each other. Moreover, high-resolution electron microscopy reveals that microsyntactic intergrowth frequently occurs in the phases with $n > 5$. The occurrence of the latter intergrowth is explained in terms of the bond length obtained.

Electron Microscope Observation of Lattice Defects in the Fe–Cr σ-phase. TSUTOMU ISHIMASA, YASUYUKI KITANO, AND YUKITOMO KOMURA, Department of Materials Science, Faculty of Science, Hiroshima University, Higashi-senda-machi, Naka-ku, Hiroshima 730, Japan. The lattice image of the Fe–Cr σ-phase was observed by high-resolution electron microscopy with the c axis of the tetragonal cell parallel to the incident beam. It was found that bright dots of the observed image correspond to the positions of atoms in the $z = \pm\frac{1}{4}$ planes of the σ-phase structure. Sequence faults were found in the irregular part of the lattice image. The analysis of the faults shows that an extra plane of $\frac{1}{2}a_0$ width is inserted into the regular structure and one side of the fault is slightly shifted parallel to the fault plane with respect to the other side, which is consistent with the model proposed by Frank and Kasper. A unit cell step of the sequence faults was found and a model of the step was proposed.

Phase Relations in the Sn–W–O Ternary System near to WO_3. THOMMY EKSTRÖM, M. PARMENTIER AND R. J. D. TILLEY, School of Materials Science, Bradford BD7 1DP, W. Yorkshire, United Kingdom. Phase relations in the Sn–W–O system for compositions near to WO_3 and temperatures up to 1173 K have been determined by electron microscopy and X-ray diffraction. The phase limits for the bronzes previously reported in this system have been determined. For the orthorhombic I bronzes the

phase limits are from $Sn_{0.04}WO_3$ to $Sn_{0.06}WO_3$. Two orthorhombic II bronze phases form, one at a composition of $Sn_{0.13}WO_3$ to $Sn_{0.15}WO_3$, and another at $Sn_{0.16}WO_3$. These bronzes have structures which consist of lamellae of WO_3 united by fault planes. The other bronze phase to form, with the tetragonal tungsten bronze structure, has a lower composition limit of $Sn_{0.21}WO_3$.

Thermodynamics of Double Oxides. II. Study of the $CoO-TiO_2$ System by the Electromotive Force Method. S. G. POPOV AND V. A. LEVITSKII, Laboratory of Chemical Thermodynamics, Moscow State University, Moscow, 117234, USSR. The emf method using an oxide–ion-conducting electrolyte has been used to determine the thermodynamic properties of $CoO-TiO_2$ system in the temperature range 1160–1420°C. Electrochemical reduction and oxidation of the electrodes showed that the compositional boundary for $CoTiO_{3-y}$ is near the composition $CoTiO_{2.85}$. Standard values of ΔH° and ΔG° of formation of $CoTiO_3$ and Co_2TiO_4 from oxides and elements, as well as entropies for these compounds, are presented and compared with the literature data. The discrepancy in ΔH° values of formation from oxides for some spinels obtained from emf and gas equilibrium data and by high-temperature solution calorimetry is discussed.

Growth of Single-Phase, Single Crystals of V_9O_{17}. H. KUWAMOTO, N. OTSUKA, AND H. SATO, School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907. Single crystals of Magnéli phase V_9O_{17} were successfully grown for the first time by a vapor transport technique utilizing $TeCl_4$ as a transport agent. No trace of syntactically intergrown V_8O_{15} could be detected in these crystals. The structure is triclinic and is homologous to other Magnéli phase compounds V_nO_{2n-1} (n = 3–8). The lattice parameters (of the reduced cell) measured are a = 7.009 Å, b = 14.518 Å, c = 5.418 Å, α = 95.5°, β = 108.9°, γ = 83.1°. This compound manifests a metal–insulator transition as in other Magnéli phase compounds. The transition temperature has been determined to be 79 K. At or below the transition point down to 16 K, at which an anomalous peak in the resistivity exists, a time dependence of resistivity at fixed temperatures is found. The existence of $V_{10}O_{19}$ was also confirmed by transmission electron microscopy in a material produced under highly nonequilibrium conditions, intergrown in the matrix of V_9O_{17} in a microsyntactic fashion. The existence of $V_{10}O_{19}$ has never been reported.

The Structure of $LaTaO_4$ at 300°C by Neutron Powder Profile Analysis. R. J. CAVA AND R. S. ROTH, Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974. $LaTaO_4$ above 175°C is orthorhombic, space group $A2_1am$, with a = 5.6643(1), b = 14.6411(3), c = 3.9457(1), and z = 4. It is isostructural with room temperature $BaMnF_4$. The structure, refined by the Rietveld powder profile analysis technique to a final agreement index of 8.6%, consists of sheets of corner-shared TaO_6 octahedra extending perpendicular to b, bonded to each other parallel to b by the 9-coordinated lanthanum ions. All atoms are in position (x, y, 0) with coordinates: La(.1788, .1676), Ta(.2192, .4141), O1(.4216, .3008), O2(−.0486, .3380), O3(.5614, .4689), O4(.2496, .9153). Orthorhombic $CeTaO_4$ and $PrTaO_4$ are isostructural.

The Crystal of Lu_3S_4: A New Population Wave Structure. A. V. HARIHARAN, D. R. POWELL, R. A. JACOBSON, AND H. F. FRANZEN, Ames Laboratory–DOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011. The monosulfide of lutetium loses lutetium preferentially upon vaporization *in vacuo* at 1750°C, and the quenched samples exhibit a new structure which is formed by an ordering of metal vacancies on the rock-salt type of lattice.

Structure cristalline de $K_2SO_4(SbF_3)_2$. MARIE BOURGAULT, BERNARD DUCOURANT, BERNARD BONNET, AND ROBERT FOURCADE, Laboratoire de Chimie Minérale D, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 Montpellier Cédex, France. The crystal structure of $K_2SO_4(SbF_3)_2$ was determined by X-ray diffraction on a single crystal (R = 0.035 for 2264 reflections). There are two families of antimony atoms showing two different environments: AX_5E octahedron (6-coordination) and AX_6E 3.3.1 monocapped octahedron (7-coordination). The SO_4^{2-} unit weakly bonded to four antimony atoms is not much distorted. This arrangement permits the minimization of $\pi-E$ interactions. Infrared and Raman spectra are discussed in terms of diffraction results.

The Crystal Structure of $Mg_{51}Zn_{20}$. IWAMI HIGASHI, NOBUHIRO SHIOTANI, M. UDA, TADASHI MIZOGUCHI, AND HIROAKI KATOH, The Institute of Physical and Chemical Research, Wako-Shi,