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Abstracts of Forthcoming Articles

Microscopic Observations on the Thermal Decomposition of α-Aluminum Hydride. P. J. HERLEY, O. CHRISTOFFERSON, AND J. A. TODD, Department of Materials Science and Engineering, State University of New York, Stony Brook, New York 11794. The various isothermal and photolytic decomposition stages of α-aluminum hydride have been examined by scanning electron microscopy. The pristine material consists of cuboids, 50–100 μm on a side, some of which are contact- or interpenetrating twins. The interpenetrating twin axis appears to be the [001] body diagonal of the cuboids. The cuboids' surface, which has been chemically treated to promote thermal stability, contains faceted pits whose sides lie along close-packed directions. The pit interiors show evidence of layering. During the thermal induction period, patches containing acicular filaments, each ~0.005 μm in diameter and ~0.3 μm in length, of Al metal are formed and are dispersed randomly on the internal crystal surfaces. During the acceleratory period, a large number of additional patches appear in which some of the filaments cluster together to form small clumps. The acicular filaments in all patches thicken and increase slightly in length as the reaction proceeds. Later in the acceleratory period, bubbles (0.2–3.5 μm in diameter) appear. The bubbles are randomly distributed throughout the cuboid and produce isolated volumes (~2 to 7 μm in diameter) of partially reacted AlH_3. Eventually, the filaments spread over the entire internal substructure of the cuboid. However, although completely decomposed, the cuboid remains intact. Preexposure to 1.0×10^9 R ^{60}Co γ-rays blackens the surface and produces a "rougher" external surface with some densely decomposed patches and many more filaments. Additional patches containing denser clusters of acicular nuclei were observed in the surface after uv photolysis at room temperature and at 150°C. At 150°C delamination of the surface layer occasionally occurs in the coirradiated material. The increased number of nuclei formed by preirradiation and uv photolysis confirm kinetic studies which postulate the presence of additional nuclei formed by the irradiation.

The Infrared Spectra, Phase Transition, and Structural Properties of Tetraethylammonium Hexafluoroantimonate $(C_2H_5)_4\,NSbF_6$. W. H. J. DE BEER, A. M. HEYNS, P. W. RICHTER, AND J. B. CLARK, National Physical Research Laboratory, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria 001, Republic of South Africa. $(C_2H_5)_4\,NSbF_6$ (TEAHFA) is face-centered cubic with $a = 11.487$ Å at ambient temperature and undergoes a first-order phase transition at 246 K on cooling and at 272 K on heating. The infrared spectra of TEAHFA confirm the cubic structure of the room temperature phase I in which no evidence could be found for the existence of hydrogen bonds between the cations and anions.

Studies on the Compounds in Ba–Fe–S System. III. Phase Relation of $Ba_{1+x}Fe_2S_4$ *with Infinitely Adaptive Structure.* N. NAKAYAMA, K. KOSUGE, AND S. KACHI, Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan. Samples of infinitely adaptive phase $Ba_{1+x}Fe_2S_4$ [or $Ba_p(Fe_2S_4)_q$; p, q: integer] were carefully prepared by changing nominal composition and annealing temperature T_a. The single-phase materials, defined in this paper as a member of the infinitely adaptive series $Ba_p(Fe_2S_4)_q$, were obtained by the addition of excess sulfur in the nominal composition range $0.05 \leq x \leq 0.20$ at T_a ranging from 650 to 880°C. X-Ray powder diffraction showed the existence of many members of the $Ba_p(Fe_2S_4)_q$ series. The supercell periodicity was markedly dependent on T_a. The composition of reaction products estimated from X-ray diffraction, a method which was proposed by Grey based on crystallographic consideration, deviated in practice from the nominal composition. This fact suggests random distribution of Ba and Fe vacancies.

Crystal Structure and Charge Carrier Concentration of $W_{18}O_{49}$. K. VISWANATHAN, K. BRANDT, AND E. SALJE, Mineralogisches Institut, Hannover, West Germany. The electrical resistivity of the tungsten oxide, $W_{18}O_{49}$, is 1.75×10^{-3} Ω cm along the needle axis. The charge carrier density, as determined by reflectivity measurements, is 1.87×10^{22} cm^{-3}, thereby indicating that most of the charge carriers are delocalized. Hence the smaller conductivity along the needle axis than that expected for such charge carrier concentrations must be found in the structure, which has been refined using the data collected with an automatic diffractometer. The structure consists of WO_6 and WO_7 polyhedra which are linked along edges and/or corners. However, as the linkage parallel to b takes place only by sharing corners, an anisotropy in the electrical conductivity may be expected. Another explanation for the smaller conductivity may be found in the occurrence of defects such as tunnels in the structure, which may scatter the electrons. The refinement shows that the tungsten positions, determined by Magneli (1949), are essentially correct; but the positions of the oxygens, especially two of them, differ considerably. This results in one of the tungsten atoms getting an additional coordinating oxygen, the coordination number thereby becoming 7.

Structure de $SnPb_2O_4$ a Quatre Temperatures Relation Entre Dilatation et Agitation Thermiques. J. R. GAVARRI, J. P. VIGOUROUX, G. CALVARIN AND A. W. HEWAT, Laboratoire de Chimie–Physique du Solide, Ecole Centrale, 92290 Chatenay Halabry, France. The structural study of $SnPb_2O_4$ oxide, an isomorphic compound belonging to the general family "MeX_2O_4" like Pb_3O_4, is made from accurate X-ray and neutron diffraction techniques on powdered samples. The structural evolution of $SnPb_2O_4$ is analyzed from 300 to 5 K: no phase transition is observed contrary to Pb_3O_4 which exhibits a quadratic → orthorhombic transition at 170 K. The thermal expansion tensor is practically isotropic in this temperature range: the α_a and α_V coefficients are neighboring those observed in the Pb_3O_4 tetragonal phase at the same temperature. On the other hand, the thermal vibrations are strongly anisotropic, with large amplitudes in the (a, b) plane. In this study we connect the thermal vibrations to the thermal expansion. $\overline{Bab}$ and $\overline{Bc}$ temperature factors are considered as functions on the a and c cell parameters. We discuss the relation established by Gruneisen between the mean square amplitudes of vibrations and the thermal volume expansion. The interatomic distances we found show that the bindings are similar to that of Pb_3O_4: only the $[S_n^{4+}O_6]$ octahedra are smaller than $[Pb^{4+}O_6]$ octahedra.

The Phase Relations in the Binary System of TiO_2–Na_2O by the Hydrothermal Reactions of TiO_2 with NaOH. MAMORU WATANABE, National Institute for Researches in Inorganic Materials, Namiki 1-1, Sakura-mura, Niihari-gun, Ibaraki, 300-31, Japan. The hydrothermal reactions of TiO_2 with NaOH were performed in the molar range of Na_2O from 0 to 30% between 250 and 530°C. The compounds obtained are TiO_2 (rutile, brookite, and anatase), $Na_2O \cdot nTiO_2$ (n = 3,4,6, and 9) and Na_xTiO_2, of which the formation ranges are shown in a reaction diagram. The roles of water in this hydrothermal system are investigated to discuss the differences among the known and the present reaction diagrams and to raise a reliability of diagrams. From the present reaction diagram, phase relations in the system TiO_2–Na_2O are estimated taking account of the direct or indirect actions of hydrothermal water on solid phases.

Structural Aspects of the Metal–Metal Interactions in the $Ti_{1+x}S_2$ Materials. E. TRONC AND R. MORET, Laboratoire de Chimie Appliquée de l'Etat Solide, ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris Cédex 05, France. Interlayer metallic interactions are shown to manifest themselves in both stacking correlations and titanium sublattice distortions. A quantitative study is reported through the structure refinement of one of the $Ti_{1.33}S_2$ superstructures. The interactions seem to involve Coulomb repulsion forces and should be valid in a broad composition range. Lattice distortions are predicted for other structures including the nonstoichiometric 1*T* structure.

Crystallography and Phase Relations of MeO–M_2O_3–TiO_2 Systems (Me = Fe,Mg,Ni; M = Al,Cr,Fe). J. HAUCK, Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, Federal Republic of Germany. Subsolidus phase relations of ternary oxide systems containing divalent Fe, Mg, or Ni; trivalent Al, Cr, or Fe; and tetravalent Ti are characterized by solid solutions at metal/oxygen ratios $\frac{3}{4}$, $\frac{2}{3}$, and $\frac{3}{5}$. At low temperatures only compounds with cubic or hexagonal close-packed oxygen and uniform oxygen coordination remain stable in the crystal structures: NaCl, spinel, ilmenite-α-Al_2O_3, TiO_2. The pseudobrookite phases $FeTi_2O_5$, $MgTi_2O_5$, Al_2TiO_5, Fe_2TiO_5; the V_3O_5-structure phase Cr_2TiO_5; and the Andersson phases $Cr_2Ti_{n-2}O_{2n-1}$ (n = 4,6,7,8,9) decompose. Additional phases with close-packed oxygen as predicted by a simple structure model for metal/oxygen ratios $\frac{7}{12}$, $\frac{5}{6}$, and $\frac{11}{12}$ do not form but presumably are important for nonstoichiometric solid solutions. Most differences between systems containing transition metals and the MgO–Al_2O_3–TiO_2 system can be attributed to crystal field effects.

Magnetic Resonance Study of $(Gd_xY_{1-x})Co_2$ Compounds. E. BURZO, MAGDA BALANESCU, AND M. CHIPARA, National Center of Physics, P.O. Box 5206, Bucharest, Romania. The results of magnetic resonance studies on ferrimagnetic $(Gd_xY_{1-x})Co_2$ compounds, both below and above the Curie points,