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Abstracts of Forthcoming Articles

The System GeO_2–FeO–Fe_2O_3 at 1000°C. E. TAKAYAMA,* N. KIMIZUKA, K. KATO, H. YAMAMURA, AND H. HANEDA, National Institute for Research in Inorganic Materials, Sakuramura, Niiharigun, Ibaraki, Japan-305. The phase diagram of the GeO_2–FeO–Fe_2O_3 system was established. Four new compounds, $Fe_{3.2}Ge_{1.8}O_8$, $Fe_9Ge_5O_{22}$, $Fe_4Ge_2O_9$, and $Fe_{10}Ge_9O_{29}$, were found in the system. The diagram is much more complex than the corresponding one of SiO_2–FeO–Fe_2O_3. The difference between the two systems may be related to the ionic radii of the cations, Ge^{4+} and Si^{4+}.

The Crystal Structure of Hydrogen Cerium(III) Sulfate Hydrate, $[H_3O]\,[Ce(SO_4)_2]\cdot H_2O$. B. M. GATEHOUSE,* AND A. PRING, Department of Chemistry, Monash University, Clayton, Victoria, Australia, 3168. $[H_3O]\,[Ce(SO_4)_2]\cdot H_2O$ crystallizes in the monoclinic system with unit-cell dimensions (from single-crystal data) $a = 9.359(4)$, $b = 9.926(4)$, $c = 8.444(3)$ Å, $\beta = 96.53(9)°$, and space group P^2_1/n, $z = 4$. The structure was solved by conventional heavy atom methods using 1787 counter-measured reflections (Mo$K\alpha$ radiation), and refined using full-matrix least-squares techniques to an R of 0.0465 ($wR = 0.0413$). The structure consists of cerium(III) ions in irregular 9-coordination to oxygen atoms from two bidentate sulfate ions, four monodentate sulfate oxygen atoms, and one water molecule. The oxonium ions are present as isolated ions in the structure and take part in the hydrogen bonding network. The Ce–O bond lengths range from 2.454(7) to 2.626(6) Å.

Structure Relationships Affecting the Stability of A15 and Ti_3P-type Compounds. R. M. WATERSTRAT, American Dental Association Health Foundation Research Unit, National Bureau of Standards, Washington, D.C. 20234. Observed interatomic distances in A15 and Ti_3P-type compounds are analyzed as deformations of ideal atomic rigid spheres. The analysis suggests that structural instabilities may develop in A15 compounds when the atomic size of the B-element becomes approximately 10% smaller than that of the A-element. These instabilities apparently originate from strong repulsive interactions along the atom chains. The internal strains associated with these interactions may be relieved by martensitic transformations, deviations from the ideal A_3B stoichiometry, addition of ternary elements, and transformation to a Ti_3P-type structure. Instability apparently develops in the Ti_3P-type compounds when the A and B element atoms are nearly equal in size. The instability in this case would result primarily from repulsive forces associated with a strong compression of the B-element atoms.

Heat Capacity and Thermodynamic Functions of the RFe_2 Compounds (R = Gd, Tb, Dy, Ho, Er, Tm, Lu) Over the Temperature Region 8 to 300 K. D. J. GERMANO, R. A. BUTERA,* AND K. A. GSCHNEIDNER, JR., Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. Experimental heat capacity data for the Laves phase RFe_2 intermetallic compounds (R = Gd, Tb, Dy, Ho, Er, Tm, and Lu) have been determined over the temperature range 8 to 300 K. The error in these data is thought to be less than 1%. Smoothed heat capacity values and the thermodynamic functions. $(H^\circ_T - H^\circ_0)$ and S°_T, are reported throughout the temperature range for the RFe_2 series. In addition, $(G^\circ_{298} - H^\circ_0)$ at 298 K is reported for all the RFe_2 compounds. These data were analyzed and it was shown that the maxima in the thermodynamic functions near $HoFe_2$ are due to the magnetic contribution of the lanthanide element. The lattice contribution to the entropy at 300 K was estimated, and from this quantity the Debye temperature was calculated to be about 300 K which is in good agreement with the low-temperature heat capacity. Furthermore, this analysis indicates that the apparent electronic specific heat constants, γ, for $TbFe_2$, $DyFe_2$, and $HoFe_2$ reported earlier are in error.

Preparation and Structure Refinement of KTi_3TaO_9 and $K_3TiTa_7O_{21}$. B. M. GATEHOUSE* AND M. C. NESBIT, Department of Chemistry, Monash University, Clayton, Victoria, 3168 Australia. KTi_3TaO_9 crystallizes in the orthorhombic system with unit-cell dimensions $a = 6.392(2)$, $b = 3.793(1)$, $c =$

Note. Asterisks indicate author to be addressed.

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14.877(4) Å, $z = 2$, and space group $Pnmm$. $K_3TiTa_7O_{21}$ crystallizes in the hexagonal system with unit-cell dimensions $a = 9.095(3)$, $c = 12.063(4)$ Å, $z = 2$ and space group $P6_3/mcm$. The structures were solved by conventional Patterson and Fourier techniques, the former using 283 unique reflections ($I \geq 3\sigma(I)$) was refined by full-matrix least-squares techniques to an R of 0.0551 ($R_w = 0.0496$), the latter using 343 unique reflections ($I \geq 3\sigma(I)$) was refined using the same technique to an R of 0.0354 ($R_w = 0.0279$). Intensity data were measured using counter methods and the "ω" scan technique. KTi_3TaO_9 is isostructural with KTi_3NbO_9 whose structure was previously derived from powder data, and $K_3TiTa_7O_{21}$ adopts the same structure as found for the nonstoichiometric phase $K_{5.5}Ta_{15.7}O_{42}$ in this laboratory. Both materials were obtained as single crystals by the use of a flux in their preparation. The distribution of titanium and tantalum over the octahedral sites is discussed relative to previously determined structures.

Kinetics and Mechanistic Aspects of the Reduction of Chromium Dioxide. R. SAEZ-PUCHE AND M. A. ALARIO-FRANCO,* Laboratoire de Cristallographie, CNRS 166 X, 38042 Grenoble Cédex, France. Thermogravimetric experiments on very small, single-crystalline, acicular particles of CrO_2, of homogeneous size and shape, indicate that the reduction of CrO_2 by hydrogen, to produce CrOOH, can be explained by means of a unidimensional diffusion mechanism. Hydrogen diffuses along the empty tunnels that exist parallel to the c-axis in the rutile-like unit cell. The corresponding diffusion equation is: $D = 10^{-6}(-19.3 \pm 2.3/RT)$ cm^2/sec, and is valid for 490 K $< T <$ 519 K and $30 < P_{H_2} <$ 110 Torr.

Rare Earth Transition Metal Sulfides, $LnMS_3$ (Ln = Rare Earth; M = Transition Metal). T. MURUGESAN, S. RAMESH, J. GOPALAKRISHNAN, AND C. N. R. RAO,* Solid State and Structual Chemistry Unit, Indian Institute of Science, Bangalore, 560012, India. Ternary rare earth–transition metal sulfides $LnMS_3$ with Ln = La, Nd, Gd, and M = V, Cr as well as Ln = La and M = Mn, Fe, Co, Ni have been prepared and characterized. The vanadium and chromium sulfides crystallize in a monoclinic layer structure isotypic with $LaCrS_3$ while the other $LnMS_3$ sulfides crystallize in a hexagonal structure. Chemical shifts of the metal K-absorption edge and XPS binding energies of core levels indicate that the transition metal is trivalent in the V and Cr sulfides, while it is divalent in the Mn, Fe, Co, and Ni sulfides. Electrical and magnetic properties of the sulfides are discussed in terms of their structure and electronic configurations of the transition metal ions.

Kationenverteilungen in einigen Zinnspinell-Mischkristallen. G. VON BECKH, P. ZEGREANU, AND M. TROMEL,* Institut fur Anorganische Chemie der Johann Wolfgang Goethe Universitat, Niederurseler Hang, D-6000 Frankfurt a.M. 50, Bundesrepublik Deutschland. In inverse tin spinels $(Mg, M)_2SnO_4$ (with M = Zn, Co, or Ni), the distribution of bivalent metal atoms was determined from samples which had been quenched from 1473 to 1073 K or cooled slowly. In Mg_2SnO_4, zinc preferentially occupies tetrahedral sites with $\Delta G°$ values of about 18 kJ/g-atom. Cobalt and magnesium are equally distributed over octahedral and tetrahedral sites, whereas nickel occupies octahedral sites only. Lattice constants of $(Mg, Zn)_2SnO_4$ solid solutions deviate largely from Vegard's law, but depend linearly on the zinc concentrations in tetrahedral and octahedral sites according to $a = c_0 + c_1$ [Zn(tetr.)] $+ c_2$ [Zn(oct.)]. Zinc in tetrahedral sites causes a lattice contraction; in octahedral sites, however, a lattice expansion.

Deuteron Magnetic Resonance and Hydrogen Bond Network of Ammonium Trihydrogen Selenite. I. S. VINOGRADOVA, L. V. Kirensky Institute of Physics, Academy of Sciences USSR, Siberian Branch, Krasnoyarsk, 660036, USSR. The DMR spectra of single-crystal $ND_4D_3(SeO_3)_2$ have been studied. The principal values and the direction cosines of field-gradient tensor of deuterons located on three nonequivalent O. . .O hydrogen bonds have been determined. The lengths of hydrogen bonds have been calculated from eQq/h values; the deuterons have been located on hydrogen bonds. The comparison with the DMR data of isomorphous compound $RbD_3(SeO_3)_2$ is made, and influence of N–H. . .O hydrogen bonds on the structural parameters of O. . .O hydrogen bonds is discussed.

Les Differentes Formes Cristallines de Y_3ReO_8: Relations avec la Structure Fluorine. G. BAUD, J.-P. BESSE, R. CHEVALIER,* AND M. GASPERIN, Equipe de Cristallographie et Physico-Chimie des Matériaux, associée au CNRS (ERA 897), Université de Clermont II, B.P. 45, 63170 Aubiere, France. The monoclinic $Y_3ReO_8\beta$ phase is synthesized at 40 kbar and 900°C. The crystal structure is solved to