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Abstracts of Forthcoming Articles

The System TiO_2–MnO_x: A Structural, Thermogravimetric and Magnetic Study. M. VALIGI AND A. CIMINO. Centro di Studio (C.N.R.) su "Struttura ed Attivita Catalitica di Sistemi di Ossidi," Istituto Chimico, Universita di Roma, Roma, Italy. The unit cell parameter variations of TiO_2 on addition of up to 8% atomic ratio of manganese oxide have been investigated. Magnetic susceptibilities in the range 98–600°K have been measured, and weight loss in hydrogen atmosphere has been recorded up to 1173°K. The results show that, at 1273°K in air, manganese is incorporated as Mn^{4+} in the TiO_2 structure up to 1.24% atomic wt. Manganese in excess (with respect to the solubility value) reacts with TiO_2 to form $MnTiO_3$. The Mn^{4+} ions in solid solution are reduced by hydrogen in the temperature range 723–923°K to Mn^{2+}, which precipitate as $MnTiO_3$.

Magnetic Behavior and Infrared Spectra of Jarosite, Basic Iron Sulfate and Their Chromate Analogs. D. A. POWERS, G. R. ROSSMAN, H. J. SCHUGAR, H. B. GRAY. Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91109. The magnetic behavior and infrared spectroscopic features of $KFe_3(SO_4)_2(OH)_6$ (jarosite), $(H_3O)Fe_3(SO_4)_2(OH)_6$ (hydronium jarosite), $KFe_3(CrO_4)_2(OH)_6$, $Fe(OH)SO_4$ (basic iron sulfate), and $Fe(OH)CrO_4$ (basic iron chromate) are reported. Spectroscopic data are in accord with X-ray data which show that $KFe_3(SO_4)_2(OH)_6$, $(H_3O)Fe_3(SO_4)_2(OH)_6$, and $KFe_3(CrO_4)_2(OH)_6$ are isostructural with $KAl_3(SO_4)_2(OH)_6$ (akunite). All the species exhibit negative deviations from Curie–Weiss behavior over the temperature range 300–76°K. The compounds $KFe_3(CrO_4)_2(OH)_6$ and $Fe(OH)CrO_4$ undergo ferrimagnetic transitions at 73 and 71°K, respectively. Maxima occur in the susceptibilities of $KFe_3(SO_4)_2(OH)_6$ and $(H_3O)Fe_3(SO_4)_2(OH)_6$ at 45 and 50°K, respectively.

Effet Jahn–Teller Cooperatif et Affinité Tetraedrique des Ions Mn^{2+} et Zn^{2+} dans le Système Mn_3O_4–Zn_2SnO_4. M. NOGUES AND P. POIX. E. R. 83 du C.N.R.S. Université de Paris XI, Laboratoire de Chimie Minérale, Bâtiment 420-91405 Orsay, France. Comparison between synthesis in air and in vacuum of the solid solution $t\,Mn_3O_4 + (1\text{-}t)Zn_2SnO_4$, and cristallographic study of the nonoxidized compounds allowed us to establish the distribution and the electronic configuration of cations in tetrahedral (A) and octahedral (B) sites. The competitive aspect of Zn^{2+} and Mn^{2+} ions to occupy tetrahedral sites is discussed. In air, the nonoxidizable character of Mn^{2+} on an A-site is clearly borne out, whereas the B-site displaced manganese oxidizes to Mn^{3+}. In vacuum, the critical concentration of Mn^{3+} ion at the octahedral site, involving a cooperative Jahn–Teller effect, is about 50%. An important fact has also been put forward: the microscopic distortion of the oxygen octahedra, which the ratio of long and short anion–cation distances expresses, is equal to the unit-cell macroscopic deformation that the ratio $c/a\sqrt{2}$ represents.

Magnetic Susceptibility of the Uranium Nitrides. R. TROC. Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland. The magnetic susceptibility of UN, and of the higher uranium nitrides has been measured over a wide temperature range, i.e., 4.2–950°K. A large temperature-independent term χ_0 equal to $310 \pm 10 \times 10^{-6}$ emu/mole has been derived from the total susceptibility data of UN. The obtained χ_M values of UN are also related to the Knight shift data from literature. For the higher nitrides U_2N_{3+x} the magnetic susceptibility has been measured for N:U ratios between 1.55 and 1.80. Antiferromagnetic phase transitions have been found for all the examined compositions. The transition temperature T_N gradually decreases as the nitrogen content increases, varying from 94°K for $UN_{1.55}$ to about 8°K for the maximum composition of $UN_{1.80\pm0.02}$. The magnetic properties of the higher nitrides are discussed in terms of mixed valency states, either U^{4+} and U^{6+} or U^{4+} and U^{5+} for the stoichiometric U_2N_3.

Oxydes de Plomb. I. Structure Cristalline du Minium, Pb_3O_4, à Temperature Ambiante (293°K). J. R. GAVARRI AND D. WEIGEL. Laboratoire de Chimie, Physique du Solide, E.R.A. au C.N.R.S.

N° 456 C.S.P. Universite Paris-Nord et Ecole Centrale des Arts et Manufactures, 92290 Chatenay-Malabry, France. The structure of Pb_3O_4 at 293°K has been refined to an R value of 0.06, using 29 neutron diffraction data obtained from a powdered sample. Oxygen atoms are displaced in the quadratic cell (space group $P4_2/mbc$; $a = 8.811$ Å and $c = 6.563$ Å) with respect to previous results obtained by several authors. The interatomic Pb^{IV}–O and Pb^{II}–O distances are compared with those found in other lead oxides. While the oxygen octahedra around Pb^{IV} atoms are characterized by bondings a little too long, the divalent lead coordination is characterized by bondings a little too short.

Optical and Electronic Properties of Some New Rare Earth-Doped Lead Sodium Apatites. L. H. BRIXNER AND P. E. BIERSTEDT. Central Research Department, E. I. duPont de Nemours and Company, Wilmington, Delaware 19898. Single crystals of the anion-deficient apatite of formula $Pb_8Na_2(PO_4)_6\phi_2$ as well as rare earth-doped compositions of the type $Ln_xPb_{8-x}Na_2(PO_4)_6\phi_{2-x/2}O_{x/2}$ with Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er have been grown by the Czochralski technique. All crystallize in the $P6_3/m$ space group of apatite with c_h about 7.20 Å and a_h about 9.73 Å. Transmission, excitation, and fluorescence spectra were obtained on many single crystals and are discussed. Anomalous dielectric behavior indicating ionic conduction is also presented. It is further shown that the often quoted "lead orthophosphate of apatite structure, $Pb_3(PO_4)_2$" is actually not pure lead phosphate but rather a sodium stabilized apatite of the composition $Pb_{8+x}Na_{2-x}(PO_4)_6\phi_{2-x/2}O_{x/2}$.

The Oxidation State of Iron in some Ba–Fe–S Phases: A Mössbauer and Electrical Resistivity Investigation of Ba_2FeS_3, $Ba_7Fe_6S_{14}$, $Ba_6Fe_8S_{15}$, $BaFe_2S_3$, and $Ba_9Fe_{16}S_{32}$. W. M. REIFF, I. E. GREY, A. FAN, Z. ELIEZER, AND H. STEINFINK. Materials Science Laboratory, Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712. Mössbauer spectroscopy, electrical resistivity, and magnetic susceptibility results are used in conjunction with crystal structure information to characterize the oxidation state of iron in 5 phases formed in the Ba–Fe–S system. The compounds have as a common feature FeS_4 tetrahedra which articulate by edge and corner sharing into infinite chains or columns. In Ba_2FeS_3 and $Ba_7Fe_6S_{14}$ iron is divalent in the first compound and in the latter the ratio of Fe(II)/Fe(III) is 2:1 as expected by stoichiometry. The electrons are localized and Fe(II) and Fe(III) are in definite locations in the trinuclear $[Fe_3S_6S_{2/2}]$ unit. Delocalization of electrons occurs in $Ba_6Fe_8S_{15}$, $BaFe_2S_3$, and $Ba_9Fe_{16}S_{32}$ and these compounds have low electrical resistivities and display only one quadrupole doublet in the room temperature Mössbauer spectrum. The isomer shift values of 0.2 mm/sec and 0.6 mm/sec are diagnostic of high spin Fe(III) and Fe(II), respectively, when they are in tetrahedral coordination with sulfur; intermediate values are found when electron delocalization occurs.

Etude par Effet Mössbauer de la Structure et des Propriétés de Diffusion de la Phase Antifluorine Non-stoechiometrique: Li_8SnP_4. J. P. MOTTE AND N. N. GREENWOOD. Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, England. The unit cell of $Li_{8+4x}Sn_{1-x}P_4$ ($-0.17 < x < +0.09$) results from an antifluorite superlattice with partial ordering of the tin atoms in space group $P\bar{4}3n$. Mössbauer spectroscopy, applied to 3 compositions ($x = -0.14$, 0, and 0.08), confirms the X-ray diffraction results with regard to tin distribution. Lithium atoms can be located on the different sites (tetrahedral and octahedral) from the fact that the isomer shift observed for the tin is a direct function of the occupation by lithium of the octahedral interstices. Mössbauer spectroscopy also establishes the characteristics of lithium diffusion in the lattice as a function of temperature and composition.

Some Thermodynamic Properties in Spinel Solid Solutions with the Fe_3O_4 Component. T. KATSURA, M. WAKIHARA, S. HARA AND T. SUGIHARA. Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan. Phase equilibria in $Fe–Fe_2O_3–Cr_2O_3$, $Fe–Fe_2O_3–V_2O_3$, $FeO–Fe_2MoO_4–Fe_3O_4$, and $FeO–Fe_2O_3–ZrO_2$ systems were precisely determined. On the basis of the present results, together with the $FeO–Fe_2O_3–TiO_2$ system studied by Taylor at 1300°C and by Webster and Bright at 1200°C, the following results were obtained (1) The solid solutions Fe_2TiO_4–Fe_3O_4, and Fe_2MoO_4–Fe_3O_4 are approximately ideal in respect to the activity–composition relation. (2) On the contrary, the solid solutions $FeCr_2O_4$–Fe_3O_4 and FeV_2O_4–Fe_3O_4 deviate significantly from Raoult's law, and these are of regular solution defined by Hildebrand.