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Abstracts of Forthcoming Articles

Pattern-Fitting Structure Refinement of Tin(II) Oxide. F. IZUMI, National Institute for Research in Inorganic Materials, 1-1 Namiki, Sakura-mura, Niihari-gun, Ibaraki 305, Japan. The Rietveld profile-analysis refinement procedure has been applied to X-ray powder diffractometer data collected from tin(II) oxide with Cu$K\alpha$ radiation. Background corrections were calculated by Aitken–Lagrange interpolation to remove errors resulting from simple linear interpolation. Four symmetric profile functions were tested; the use of a modified or intermediate Lorentz function led to a more satisfactory fit than use of the Gauss or Lorentz function. A preferred-orientation function proposed by Toraya and Marumo gave lower R values than that of Rietveld. The positional parameter of the tin atom was found to be 0.2369, which is almost identical with the corresponding value reported for isomorphous lead(II) oxide.

Cd Diffusion into PbTe. E. SILBERG, Y. STERNBERG, AND N. YELLIN,* Solid State Physics Department, Soreq Nuclear Research Centre, Yavne, Israel. Cadmium diffusion into p-type PbTe wafers and out of n-type Cd-diffused PbTe wafers was studied. The electrical properties and Cd content of the wafers showed that only about 150 ppm of the diffused Cd affects the electrical properties of PbTe. The fact that most of the diffused Cd has no effect on the electrical properties of the material is explained on the basis of two different processes of Cd incorporation into the PbTe crystal.

Structure Cristalline du Vanadate mixte $In_{0.6}Li_{1.2}VO_4$. M. TOUBOUL* AND P. TOLEDANO, Laboratoire de Chimie Structurale des Materiaux, Universite P. et M. Curie (Paris VI), Bat.F-4, place Jussieu, 75230 Paris Cedex 05, France. A mixed vanadate $In_{0.6}Li_{1.2}VO_4$ has been synthesized from an equimolecular mixture of $InVO_4$ and Li_3VO_4. The exact chemical formula has been determined by a crystal structure refinement. Crystallographic data are: a = 5.763 (1), b = 8.742 (2), c = 6.385 (3) Å, Z = 4, d_{calcd} = 3.97 g · cm^{-3}. The 726 reflections have been used for structure determination and refinement, to a final value R = 0.019, after absorption and extinction corrections. InO_6 octahedra and VO_4 tetrahedra are linked together in the same three-dimensional network existing in $InVO_4$. Nevertheless, a partial substitution of In^{3+} by Li^+ and an insertion of Li^+ in tetrahedral interstices occur. Vacancies exist, either in the octahedral and tetrahedral positions, $In_{0.6}Li^{(6)}_{0.3}\square^{(6)}_{0.1}Li^{(4)}_{0.9}\square^{(4)}_{0.1}VO_4$, or solely in the tetrahedral positions, $In_{0.6}Li^{(6)}_{0.4}Li^{(4)}_{0.8}\square^{(4)}_{0.2}VO_4$.

Recherche d'une description structurale des decompositions endothermiques Solid 1 → Solide 2 + Gaz. II. Caracteristiques structurales de la reaction $2[H_2C_2O_4, BaC_2O_4, 2H_2O] \rightarrow Ba(HC_2O_4)_2, BaC_2O_4, 2H_2O + H_2C_2O_4 + 2H_2O$. J. C. MUTIN* AND Y. DUSAUSOY, Laboratoire de Recherches sur la Reactivite des Solides, Faculte des Sciences Mirande, BP 138, 21004 Dijon Cedex, France. The structure of the oxalate $H_2Ba_2(C_2O_4)_3 \cdot 2H_2O$ was established and compared with that of the oxalate $H_2Ba(C_2O_4)_2 \cdot 2H_2O$. The two acid salts were different: the first is composed of $(HC_2O_4)^-$ and $(C_2O_4)^{2-}$ ions with the formula $Ba(HC_2O_4)_2 \cdot BaC_2O_4 \cdot 2H_2O$; the second is composed of $H_2C_2O_4$ molecules and $(C_2O_4)^{2-}$ ions, with the formula $H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$. Simple relations between the unit-cell parameters of the two salts exist. It is shown that after elimination of alternate $H_2C_2O_4$ molecules in the structure of the $H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$ oxalate and after small movements of (C_2O_4) groups and Ba^{2+} ions, the stacking of the $Ba(HC_2O_4)_2 \cdot BaC_2O_4 \cdot 2H_2O$ oxalate can be deduced. The atomic movements and the behavior of acid functions are described. A solid–solid reaction between oxalic acid and $Ba(HC_2O_4)_2 \cdot BaC_2O_4 \cdot 2H_2O$ shows that the more acid oxalate $H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$ is a true solid solution of $H_2C_2O_4$ acid in the less acid salt.

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$Pb_4Fe_3O_8Cl$: Synthesis, Crystal Structure, and Thermal Expansion. J. Pannetier* and P. Batail, Institut Max Von Laue-Paul Langevin, Avenue des Martyrs, 156X, 38042 Grenoble Cedex, France. $Pb_4Fe_3O_8X$ (X = Cl and/or Br) was prepared by solid-state reaction. The structure of $Pb_4Fe_3O_8Cl$ was refined from X-ray single-crystal data in the centrosymmetric space group $P4/mmm$ (a = 3.9097(2), c = 15.2873(17); it can be described as an interlayering of incomplete perovskite-like sheets ($Pb_4Fe_3O_8$) with sheets of Cl. Fe(1) has a fivefold square pyramidal coordination while Fe(2) is in a regular octahedron of oxygen. Thermal expansion was measured from 25 to 500°C.

Low-Dimensionality Magnetic Interactions in the Linear Chain Transition Metal Complexes M(2,2′-Bipyridine) $(H_2O)_2SO_4$, M(Fe, Ni, and Cu). C. Nicolini and W. M. Reiff,* Department of Chemistry, Northeastern University, Boston, Massachusetts 02115. The magnetic susceptibilities of polycrystalline samples of the chain compounds M(2,2′-bipyridine) $(H_2O)_2SO_4$ (M = Fe, Ni, and Cu) have been measured in the temperature range 1.7 to 300 K. The iron and nickel compounds exhibit broad maxima in χ'_M vs T at ~8 K. The experimental results can be interpreted in terms of antiferromagnetic linear-chain systems and provide information on the magnitude of the intrachain interactions. Zero-field Mössbauer spectra of a powder sample of *trans*-μ-sulfato-diaquo(2,2,′-bipyridine)iron(II) over the preceding range were also determined. The chemical isomer shift value corresponds to six-coordinate high-spin iron(II). Below 2.0 K the compound exhibits magnetic hyperfine splitting, suggesting long-range, three-dimensional ordering with a critical temperature of $T_N \leq 1.7$ K. By means of Oguchi's Green's function theory and the experimentally determined transition temperature T_N, an estimate of the ratio of the inter- to intrachain exchange interaction is obtained.

The Vibrational Spectra and Crystallographic Properties of $CsPF_6$. A. M. Heyns, P. W. Richter, and J. B. Clark,* National Physical Research Laboratory, CSIR, P.O. Box 395, 0001 Pretoria, South Africa. $CsPF_6$(I) at ambient conditions is cubic with a possible space group of $Fm3m$-O_h^5. The Raman spectra of $CsPF_6$(I) are consistent with a disordered model in which the PF_6^- ions are tilted away from the crystallographic axes. The phase transition which occurs below 90 K in $CsPF_6$ is reflected in the vibrational spectra and further significant changes occur below 60 K in particularly the Raman bands. It is not yet clear whether these changes represent the establishment of long-range order or whether a further phase of $CsPF_6$ exists below 60 K. A possible structure for $CsPF_6$ at very low temperatures is discussed.

Interactions Magnetiques dans des Groupements Binucleaires $[Fe_2O_7]^{8-}$ au Sein de $Na_8Fe_2O_7$. H. Kessler* and Son Ly, Laboratoire de Chimie Minerale Appliquee, Ecole Nationale Superieure de Chimie, 3, rue Alfred Werner, 68093 Mulhouse Cedex, France. The magnetic interaction in the structural units $[Fe_2O_7]^{8-}$, built of two corner-sharing FeO_4 tetrahedra, in $Na_8Fe_2O_7$ (Na_2O/Fe_2O_3 = 4/1) has been studied by magnetic susceptibility measurements (4.2–500 K). An exchange integral J/k_B of −37 K is obtained by comparison of the experimental values and the calculated ones using a Heisenberg–Dirac–Van Vleck type Hamiltonian $\mathcal{H} = -2JS_1S_2$. The hypothesis of magnetically isolated $[Fe_2O_7]^{8-}$ groups is corroborated by Mössbauer spectroscopy between 1.5 and 77 K. The susceptibility measurements of the solid solutions $Na_8Fe_{2-x}M_xO_7$ (M = Al, Ga; $0 \leq x \leq 0.2$ for Al; $0 \leq x \leq 2$ for Ga) leads to the same conclusion of the existence of isolated Fe^{3+}–Fe^{3+} pairs in $Na_8Fe_2O_7$. The type of substitution of Fe by Al or Ga is determined; homonuclear Fe^{3+}–Fe^{3+} and M^{3+}–M^{3+} pairs and heteronuclear Fe^{3+}–M^{3+} pairs are formed.

The Crystal Structure of $Ca_3Cu_3(PO_4)_4$. J. B. Anderson, E. Kostiner,* and F. A. Ruszala, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268. Single crystals of $Ca_3Cu_3(PO_4)_4$ synthesized hydrothermally at 420°C and 55 kpsi (3.8 kbar) were found to occur in the space group $P2_1/a$ (No. 14) with a = 17.619(2), b = 4.8995(4), c = 8.917(1) Å, β = 124.08(1)°, and Z = 2. Full-matrix least-squares refinement of the structure using diffractometer data converged to a final anisotropic R = 0.037 (R_w = 0.046). The two calcium atoms are in six- and nine-coordination and the two copper-containing polyhedra (four- and five-coordinated) are similar to those previously found in $Cu_3(PO_4)_2$.

On the Luminescence of Titanium-Doped Lithium Zirconate (Li_2ZrO_3). G. A. M. DALHOEVEN AND G. BLASSE,* Physical Laboratory, State University, P.O. Box 80.000, 3508 TA Utrecht, The Netherlands. The luminescence of Li_2ZrO_3–Ti is described. The emission and excitation spectra are reported. The temperature dependence of the decay time is discussed and points to a complicated energy-level scheme. Further, the decay time of the luminescence of ZrO_2–Ti has been measured. It appears to be very long (~I msec).

Proprietes magnetiques et etude par spectroscopie Mössbauer des tellurites de fer $Fe_2Te_3O_9$ *et* $Fe_2Te_4O_{11}$ *structure magnetique de* $Fe_2Te_4O_{11}$ *A 4.2 K*. J. C. JUMAS,* L. FOURNES, M. WINTENBERGER, AND E. PHILIPPOT, Laboratoire de Chimie Minerale C, USTL, Place Eugene Bataillon, 34060 Montpellier Cedex, France. Magnetic study and Mössbauer resonance measurements of the tellurites $Fe_2Te_3O_9$ and $Fe_2Te_4O_{11}$ characterize antiferromagnetic ordering. The transition temperatures determined by Mössbauer resonance are 34 and 27 K, respectively. At 295 K the values of chemical shifts, 0.35 and 0.39 mm/sec, are typical of high-spin Fe(III) in octahedral coordination. Neutron powder diffraction was used to determine the magnetic structure of $Fe_2Te_4O_{11}$ at 4.2 K. It shows antiferromagnetic interactions between Fe^{3+} ions belonging to $[Fe_2O_{10}]$ groups. The magnetic space group is $P_{2a}2_1/c$.

Phase Relationships in the Systems SmH_2–SmH_3 *and* SmD_2–SmD_3. O. GREIS,* P. KNAPPE, AND H. MULLER, Institute of Mineralogy and Petrography, University of Heidelberg, Im Neuenheimer Feld 236, D-6900 Heidelberg 1, Federal Republic of Germany. The phase relationships in the system SmH_2–SmH_3 have been reinvestigated. Contrary to the literature the phase widths of SmH_2 and SmH_3 are significantly less extended: $SmH_{1.95-2.30}$ (cubic, fluorite-related) and $SmH_{2.82-2.90}$ (hexagonal, tysonite-related). In addition, a new intermediate phase of the composition Sm_3H_7 has been found. This tetragonally distorted fluorite-related phase is similar to the superstructure phase Sm_3F_7 with regard to the crystal data of the basic structure and the anion/cation ratio. Systematic phase investigations were carried out also in the system SmD_2–SmD_3 leading to analogous results. The present work shows that the phase relationships in rare-earth hydrides and deuterides are closely related to those of the systems SmF_2–SmF_3 and EuF_2–EuF_3.

Chevrel Phases. An Analysis of Their Metal–Metal Bonding and Crystal Chemistry. J. D. CORBETT, Ames Laboratory-DOE, Department of Chemistry, Iowa State University, Ames, Iowa 50011. A useful measure of the total Mo–Mo bonding in diverse phases containing Mo_6Y_8-type clusters (Y = S, Se, Cl, Br) is given by the Pauling bond order sum per electron (PBO/e). These fall into two classes: (a) strongly bonded examples with PBO/e values near 1.00 which contain either discrete clusters with extra outer (exo) atoms or infinite confacial clusters, and (b) the rhombohedral Mo_6Ch_8 and $M_xMo_6Ch_8$ Chevrel phases with reduced PBO/e values of 0.72–0.84 in which face-capping chalcogenide (Ch) must also fill exo positions. The matrix effect in the latter which is responsible for the reduced bond orders arises from a combination of particularly strong Mo–Ch intercluster bonds and closed shell Ch–Ch repulsions [3.31 Å (S), 3.38 Å (Se)] which force an elongation of the Mo_6 trigonal antiprism and reduce the Mo–Mo bonding. There is no distinction between sulfide and selenide Chevrel phases in the degree of total Mo–Mo bonding as expressed in bond orders. Changes in the structure on reduction are analyzed; the major effects come from loosening of the intercluster Mo–Ch bonding and thence a decreased distortion (matrix effect) together with a flexing of the Mo_6Ch_8 host according to the size and charge of M. Distance considerations indicate substantial covalency between M and $Ch2$, especially with Pb and Ag, while cell volumes and Mo–$Ch2$ distances suggest significant constriction occurs in phases with higher charged M, possibly owing to compression by the host lattice and coulombic contributions to binding. Evidence for Mo–M bonding with M = Fe, Co, Ni is also noted. Intercluster interactions and Mo–Mo bonding in $Mo_6S_6Br_2$ and in the mixed Mo_6Ch_8–Mo_nCh_m (n = 9, 12) cluster phases are quite consistent with those in the Chevrel phases, the total Mo–Mo bonding per electron increasing with cluster condensation owing principally to reduced Ch–Ch repulsions.

Valence State of the Fe Ions in $Sr_{1-y}La_yFeO_3$. M. TAKANO,* J. KAWACHI, N. NAKANISHI, AND Y. TAKEDA, Department of Chemistry, Faculty of Science, Konan University, Kobe 658, Japan. The $\mathrm{Sr}^{2+}_{1-y}\mathrm{La}^{3+}_{y}\mathrm{FeO}_3$ system with $0.1 \leq y \leq 0.6$ has been studied mainly by the Mössbauer effect. The results are discussed referring to the $\mathrm{Ca}_{1-x}\mathrm{Sr}_x\mathrm{FeO}_3$ system. The following four kinds of electronic phases have been observed: the paramagnetic and the antiferromagnetic average valence phases and the corresponding mixed valence phases. Two kinds of Fe ions coexist, in general, in the mixed valence phases. In the antiferromagnetic mixed valence phase, typically at 4 K, the magnetic hyperfine field and the center shift each takes a wide range of value depending on the composition, while a beautiful correlation is kept between them. The extreme values are close to those expected for Fe^{3+} and Fe^{5+}. The appropriate chemical formulas are, therefore, $\mathrm{Ca}_{1-x}\mathrm{Sr}_x\mathrm{Fe}^{(3+\Delta)+}_{0.5}\mathrm{Fe}^{(5-\Delta)+}_{0.5}\mathrm{O}_3$ and $\mathrm{Sr}_{1-y}\mathrm{La}_y\mathrm{Fe}^{(3+\delta)+}_{(1+y)/2}\mathrm{Fe}^{(5-\delta)+}_{(1-y)/2}\mathrm{O}_3$.

The Preparation and Crystal Structure of a $BaRhO_3$ Polytype. B. L. CHAMBERLAND* AND J. B. ANDERSON, Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268. Barium rhodium oxide, BaRhO_3, was prepared at 1175°C and 60–65 kbar by the reaction of BaO_2 and RhO_2. A hexagonal black platelet obtained in the reaction product was found to possess a four-layer stacking sequence in space group $P6_3/mmc$ having hexagonal unit cell parameters a = 5.744 (1), c = 9.643(1) Å. The structure was determined from 707 independent reflections of which 224 were considered observed. Averaging equivalent reflections yielded 132 unique, observed reflections. Refinement of the structure by least-squares methods gave a conventional R value of 4.4%. The structure consists of a four-layer stacking sequence of close-packed BaO_3 layers containing tetravalent rhodium in all the octahedral oxygen interstices. The compound was found to be isostructural with previously reported BaMO_3 phases. This is the first single-crystal refinement of the 4H polytype using a four-circle diffractometer.

Oxygen Defect K_2NiF_4-Type Oxides: The Compounds $La_{2-x}Sr_xCuO_{4-x/2+\delta}$. N. NGUYEN, J. CHOISNET, M. HERVIEU, AND B. RAVEAU,* Laboratoire de Cristallographie et Chimie du Solide, Universite de Caen, 14032 Caen Cedex, France. Oxygen defect $\mathrm{K}_2\mathrm{NiF}_4$-type oxides $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{CuO}_{4-x/2+\delta}$ have been synthesized for a wide composition range: $0 \leq x \leq 1.34$. From the X-ray and electron diffraction study three domains have been characterized: orthorhombic compounds with $\mathrm{La}_2\mathrm{CuO}_4$ structure for $0 \leq x \leq 0.10$, tetragonal oxides similar to $\mathrm{LaSrCuO}_4$ for $0.10 \leq x < 1$, and several superstructures derived from the tetragonal cell ($a \simeq n \cdot a_{\mathrm{LaSrCuO}_4}$ with n = 3,4,4.5,5,6) for $1 \leq x \leq 1.34$. The compounds corresponding to $0 \leq x \leq 1$ differ from the other oxides in that they are characterized by the presence of copper with two oxidation states: 2+ and 3+. A model structure for $\mathrm{La}_{0.8}\mathrm{Sr}_{1.2}\mathrm{Cu}_{3.4}$, in which copper has only the 2+ oxidation state, and for which the actual cell is tetragonal—a = 18.80_4 Å and c = 12.94 Å—has been established. The particular structural evolution of these compounds is discussed in terms of a competition between the capability of Cu(II) to be oxidized to Cu(III) and the ordering of oxygen vacancies.

Crystal Structure and Ionic Conductivity in $Na_4Zr_2Si_3O_{12}$. D. TRAN QUI, J. J. CAPPONI, J. C. JOUBERT,* AND R. D. SHANNON, Laboratoire de Cristallographie, 166 X, 38042 Grenoble Cedex, France. Na ion conductivities of $\mathrm{Na}_{4-x}\mathrm{Zr}_2\mathrm{Si}_{3-x}\mathrm{P}_x\mathrm{O}_{12}$ range from 3.5×10^{-4} $(\Omega - \mathrm{cm})^{-1}$ for x = 0 to 1.9×10^{-1} $(\Omega - \mathrm{cm})^{-1}$ for x = 1.0 at 300°C. Structure refinements of single-crystal $\mathrm{Na}_4\mathrm{Zr}_2\mathrm{Si}_3\mathrm{O}_{12}$ were carried out at 25, 300, and 620°C. Little change occurs in bond distances and angles in the $(\mathrm{Zr}_2\mathrm{Si}_3\mathrm{O}_{12})^{4-}$ framework whereas the Na(1)–O_6 and Na(2)–O_8 polyhedra enlarge dramatically with increase of temperature. The large thermal motion of Na(1) and Na(2) is probably related to the Na mobility in this structure. Of the four possible Na ion pathways, only two have openings large enough to allow reasonable mobility. The first, connecting a Na(1) site to a Na(2) site, is somewhat smaller (1.86 Å) than a Na ion (2.30 Å) at RT but increases substantially to 2.22 Å at 620°C. The second, connecting a Na(2) site to a Na(2) site, is larger (2.37 Å) and increases to 2.66 Å at 620°C. Difference Fourier maps show significant electron density along Na(2)–Na(2) paths and Na(2) thermal ellipsoids have major axes close to these paths.

Coordination and Bonding in Fe_3P–Ti_3P–V_3S–Ta_3As-Type Compounds. The Crystal Structures of Hf_3Sb and h-Ta_3Ge. J.-O. WILLERSTRÖM AND S. RUNDQVIST,* Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden. Interatomic distances in Hf_3Sb and *h*-Ta_3Ge (Fe_3P-type structure, space group $I\bar{4}$, $Z = 8$) have been determined by crystal structure refinements based on Rietveld-type full-profile analyses of Guinier–Hägg X-ray powder film intensity data. The results, together with data from the recently refined Hf_3As and Ta_3As structures, are included in a survey of coordination and bonding in Fe_3P–Ti_3P–V_3S–Ta_3As-type compounds. It is shown that the trends in atomic coordination observed can be explained in terms of an interplay of *d–d* and *d–p* electronic interactions.

Structural Relationships in Tetrahedral Frameworks: Reflections on Cristobalite. S. HANSEN, L. FÄLTH, AND S. ANDERSSON,* Inorganic Chemistry 2, Chemical Center, Box 740, S-220 07 Lund 7, Sweden. Twinning on the unit cell level of the idealized cristobalite structure, using a mirror plane as the twin and composition plane, provides a simple relationship between 14 tetrahedral frameworks. Of these, 9 are found among the aluminosilicates with examples ranging from (stuffed) silicas to zeolites and include the framework types of nepheline hydrate I, zeolite Li-A(BW), gismondine, phillipsite, merlinoite, tridymite, paracelsian, and monoclinic $CaAl_2Si_2O_8$. Similar twinning relates the frameworks of natrolite, thomsonite, and edingtonite.