Abstracts of Forthcoming Articles

Propriétés Électriques du trioxyde de tungstène a proximite de sa composition stoechiométrique. Influence des conditions thermodynamiques de preparation et phenoménès de trempe. J. P. BONNET, J. F. MARUCCO, M. ONILLON,* AND P. HAGENMULLER, Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351, cours de la Libération, 33405 Talence Cédex, France. The experimental study of variations in electrical conductivity of WO_{3-x} vs oxygen partial pressure and temperature shows evidence of interstitial W_i^{6+} as being the major defect. Under certain conditions, point defects can order themselves in extended defects. The behavior of electrical conductivity can be interpreted in terms of thermodynamic equilibrium between point defects and extended defects, the latter leading to structural modifications beyond a certain departure from stoichiometry. Moreover, WO_{3-x} shows evidence of quenching phenomena allowing electrical features characteristic of high temperatures to be kept down to room temperature. These properties may explain discrepancies among previous data.

Mechanism of the Powder Reaction between $CuSO_4(s)$ and PbO (α and β): A Thermoanalytical and Mass Spectrometric Study. E. GARCIA-CLAVEL, I. TEJEDOR TEJEDOR,* AND H. G. SANZ, Sección de Termoanálisis y Reactividad de Sólidos, Departamento de Química Analítica del CSIC, Facultad de Ciencias Químicas, Ciudad Universitaria, Madrid-3, Spain. Thermoanalytical studies and isotopic analysis of oxygen has been used to establish the actual mechanism of the $CuSO_4/(\alpha,\beta)PbO$ $1/1M$ exchange reaction (the reactants are fine powders). Whether SO_3 is or is not involved in the reaction process depends on the crystalline form of PbO, and, in the case of α-PbO, on the type of heating. Oxygen isotope analysis, carried out on reaction products when PbO is enriched in ^{18}O and when gaseous SO_3 plays no part in the process, shows that both cationic and oxygen transport are involved in the reaction mechanism.

A Structural Explanation for the Polymorphism of the α Form of Anhydrous Vanadyl Phosphate. M. TACHEZ,* F. THEOBALD, AND E. BORDES, Laboratoire de Chimie-Physique, Université de Franche-Comté, 25030 Besançon Cedex, France. According to the method of preparation of α-VOPO$_4$, the X-ray powder patterns and the cell parameters are different. A structural distinction between α_I and $_{II}$-VOPO$_4$ is proposed that is based on the relative positions of the vanadium and phosphorus atoms: in the case of α_I-VOPO$_4$ (as for α VOSO$_4$), prepared by dehydration of VOPO$_4 \cdot 2H_2O$, these atoms are on the same side of the equatorial chain V–O(2)–P–O(2)–V; therefore, its characteristic layered texture is reinforced. In the α_{II} form, these atoms are on alternate sides of that chain.

Structure cristalline de $CsYb_3F_{10}$ composes isotypes. S. ALÉONARD,* M. TH. ROUX, B. LAMBERT, Laboratoire de Cristallographie, CNRS, B.P. 166 X, 38042 Grenoble Cedex, France. Cesium ytterbium fluoride, $CsYb_3F_{10}$, crystallizes in the monoclinic system, with parameters $a = 4.2893(2)$ Å, $b = 6.7437(4)$ Å, $c = 16.196(2)$ Å, $\beta = 90°$, $Z = 2$ and space group Pc. The structure has been solved by three-dimensional Patterson and Fourier syntheses and refined by a least-squares method. For 1406 independent reflections recorded on an automatic four-circle diffractometer ($\lambda AgK\alpha$), the final R value is 0.031 ($R_w = 0.034$). Three edge-sharing pentagonal bipyramids surrounding three ytterbium atoms form Yb_3F_{17} groups and the structure is described by the superposition, according to the sequence AAA . . . , of identical sheets of edge- and corner-sharing Yb_3F_{17} groups. In these sheets, Yb atoms are located at the lattice points of a pseudo-hexagonal network. The nonoccupancy of some of these lattice points creates tunnels, perpendicular to the sheets, in which cesium atoms are located. Lattice parameters of isotypic compounds are given.

A Kinetic Study of the Oxidation of ζ-Phase Praseodymium Oxide: $(10/9)Pr_9O_{16} + (1/9)O_2 \rightarrow Pr_{10}O_{18}$. T. SUGIHARA, S. H. LIN, AND L. EYRING,* Department of Chemistry and the Center for Solid State Science, Arizona State University, Tempe, Arizona 85287. Kinetic and thermodynamic studies of the oxidation of ζ ($n = 9$ in Pr_nO_{2n-2}) to ϵ ($n = 10$) phase have been carried out using a thermogravimetric technique. The experiments covered a temperature range of 464°C to 503°C and oxygen pressure varied from 0.01 to 50 Torr. The existence of a reproducible hysteresis loop which

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depends on the temperature and pressure is shown. Measurements of the oxidation rate under isothermal conditions were fitted to different rate equations and have been found to be well represented by the equation $f = 1 - (1 - kt)^3$. This fact indicated that the process of oxidation was predominantly controlled by the chemical reaction at the interface. The activation energy for the reaction has been calculated to be 15.9 kcal/mole.

Application of the Nuclear Magnetic Resonance to the Study of the Superficial Constitutive Water of Anatase. M. A. ENRIQUEZ, C. DORÉMIEUX-MORIN,* AND J. FRAISSARD, Laboratoire de Chimie des Surfaces, Université P. et M. Curie, Tour 55, 4 Place Jussieu, 75230 Paris Cédex 05, France. The superficial constitutive water of anatase has been studied by NMR in "rigid-lattice" conditions. Spectra interpretation by shape function calculation leads to a distribution of protons between molecular water and OH groups and to characteristic distances between protons. OH groups cover all the available surface of the most hydrated sample and the water molecules are attached to the OH groups. Models of the coverage of the principal surface planes are studied by associating the NMR results with reasonable assumptions concerning the physicochemical properties of these planes. The (001) plane is the most prevalent. The OH groups occupy two different sites corresponding to overall charges of opposite sign. A description of the dehydration mechanism has been tested by considering the behavior of the model in terms of the total equivalent concentration of water.

Luminescence de l'europium divalent dans les composes α et β-RbLu$_3$F$_{10}$. A. ARBUS, M. T. FOURNIER, AND A. VEDRINE,* Groupe de Cristallographie et de Chimie des Solides, Université de Clermont II, B.P. 45, 63170 Aubiere, France. The effect of the crystal structure upon the luminescence of the divalent europium within the RbLu$_3$F$_{10}$ dimorphous matrix has been investigated. The obtained results essentially show that the difference between the rubidium coordination numbers in both α- and β-RbLu$_3$F$_{10}$ phases (15 or 16 and 8 or 10 respectively) is responsible for the changeover from a $4f^7 \rightarrow 4f^7$ emission to a $4f^65d^1 \rightarrow 4f^7$ emission.

The Six-Layer Structure of BaSn$_{0.9}$Fe$_{5.47}$O$_{11}$. M. C. CADEE* AND D. J. W. IJDO, Section of Solid State Chemistry, Gorlaeus Laboratories, Leiden State University, P.O. Box 9502, 2300 RA Leiden, The Netherlands. The crystal structure of BaSn$_{0.9}$Fe$_{5.47}$O$_{11}$ was determined using neutron powder diffraction data and the profile refinement method. The hexagonal compound, space group $P\bar{3}m1$, has *hcc*-stacked BaO$_3$ and O$_4$ layers. A new building unit for this type of structure is introduced, the Q-block with formula Ba$_2M_7$O$_{14}$, consisting of two *c*-stacked BaO$_3$ layers and two O$_4$ layers. Between the BaO$_3$ and O$_4$ layers one tetrahedral and one octahedral site is occupied, between the BaO$_3$ layers there are no other cations. BaSn$_{0.9}$Fe$_{5.47}$O$_{11}$ shows a magnetic behavior with an ordering temperature T_c of 420 K. Starting models for the structure determination were derived from the known structures of hexagonal ferrites and related compounds. Several isomorphs with formula Ba$_2$Sn$_2M^{2+}$Fe$_{10}$O$_{22}$ could be prepared, in which a partial substitution of Fe by Ga is possible. The nonstoichiometry of BaSn$_{0.9}$Fe$_{5.47}$O$_{11}$ can be explained by the surplus of positive charge if the available tetrahedral and octahedral sites of the structure are completely occupied with Sn^{4+} and Fe^{3+}. To achieve charge compensation either the occupation rates of Sn^{4+} and Fe^{3+} have to be lowered or a divalent ion has to be introduced, as is effected in the isomorphs.

Electrical Resistivities of Single-Crystal PrTiO$_3$ and NdTiO$_3$. Magnetic Properties of PrTiO$_3$, NdTiO$_3$, PrScO$_3$, and NdScO$_3$. D. A. MACLEAN, K. SETO, AND J. E. GREEDAN,* Institute for Materials Research and Department of Chemistry, McMaster University, Hamilton, Canada L8S 4M1. Electrical resistivities were measured as a function of temperature in the range below 300 K for single-crystal samples of PrTiO$_3$ and NdTiO$_3$. Both materials are semiconductors with room temperature activation energies of 0.03 to 0.04 eV. Magnetic susceptibilities for PrTiO$_3$ and NdTiO$_3$ follow the Curie–Weiss law at high temperatures with $C_m = 1.73(3)$ and $\theta_c = -49(3)$ K (PrTiO$_3$) and $C_m = 1.77(3)$, $\theta_c = -35(3)$ K (NdTiO$_3$). For PrScO$_3$ and NdScO$_3$, isostructural materials, magnetic-susceptibility data also follow the Curie–Weiss law with $C_m = 1.34(3)$ and $\theta_c = -8(2)$ K (PrScO$_3$) and $C_m = 1.51(3)$, $\theta_c = -32(3)$ K (NdScO$_3$). Assuming that the data for PrScO$_3$ and NdScO$_3$ represent a fair approximation to the rare-earth-only susceptibility, a Ti(III) contribution to the susceptibilities of PrTiO$_3$ and NdTiO$_3$ can be estimated and these are found to be near the spin-only value. PrTiO$_3$ shows complex magnetic order below 96(2) K, while NdTiO$_3$ shows no obvious sign of order above 4.2 K.

Fe₂PO₅, Un phosphate de fer de valence mixte. Préparation et Études structurale, Mössbauer et magnétique. A. MODARESSI, A. COURTOIS, R. GERARDIN, B. MALAMAN, AND C. GLEITZER,* Laboratoire de Chimie du Solide Minérale, Université de Nancy I, 54037 Nancy Cedex, France. Fe_2PO_5 is prepared from diverse components of the Fe–P–O system at 900°C in sealed silica tubes under vacuum. The study of a single crystal shows an orthorhombic cell, space group *Pnma*, with $a = 7.378$, $b = 6.445$, $c = 7.471$ Å and $Z = 4$. The structure is determined through direct methods and Fourier syntheses and refined to $R = 0.027$. The phosphorus fills isolated tetrahedra. The Fe^{II} and Fe^{III} ions are ordered in distorted octahedra: the octahedra surrounding Fe^{II} build strings parallel to the b axis and share edges; the octahedra containing Fe^{III} are connected on both sides of these strings alternatively with the PO_4 tetrahedra. The two types of octahedra share one face. Such an arrangement strongly recalls two out of the three Al_2SiO_5 polymorphs, namely, the kyanite and sillimanite. The Mössbauer spectroscopy exhibits a magnetic transition at 220 K. Below, the spectrum shows a six-line hyperfine pattern for Fe^{III} and an eight-line one for Fe^{II} with a rather weak hyperfine field; above, there are two doublets, well differentiated confirming the absence of electronic charge transfer at room temperature. The magnetic susceptibility, recorded from 90 to 300 K, is typically that of an antiferromagnetic compound with $C_M = 7.12$, $\theta_p = -350$ K and $T_N \sim 250$ K. The magnetic interactions are discussed. The electronic localization is explained through structural and crystal field considerations; the electrostatic potential difference between the Fe^{II} and Fe^{III} sites is calculated.

Critical Examination of Ga₂Se₃ Phase Equilibria. J. C. MIKKELSEN, JR., Xerox Palo Alto Research Center, Palo Alto, California 94304. The Ga_2Se_3 phase equilibria were examined by DTA, X-ray diffractometry, visual observation, and isothermal crystal growth to resolve discrepancies in the reported binary phase diagrams. The Se-rich solid solubility extends to less than 60.5 at.% Se. There is no peritectic transformation at 880°C, nor is there a liquid immiscibility from 75 to 85 at.% Se. The rate of crystal growth influences the incorporation of lattice defects and thus determines which polymorphic form of Ga_2Se_3 crystallizes from the melt. The preferred liquidus curve from 60 to 100 at.% Se is presented and compared to those reported in the literature.

²D and ¹³³Cs NMR Study of the Hydrogen Bond Network and Antiferroelectric Phase Transition of Cesium Trihydrogen Selenite. I. S. VINOGRADOVA, L.V. Kirensky Institute of Physics, Academy of Sciences, USSR Siberian Branch, Krasnoyarsk 660036, USSR. The ^2D and ^{133}Cs NMR spectra of deuterated and protiated single crystals of antiferroelectric cesium trihydrogen selenite have been studied in the high- and low-temperature phases. The number of chemically nonequivalent hydrogen bonds, their lengths, and directions in the unit cell were determined from deuteron electric field gradient tensors. The deuterons of centered hydrogen bonds have been found disordered in the paraelectric phase over two equivalent sites on either side of a center of symmetry. The antiferroelectric phase transition is accompanied by order–disorder phenomena of the H system and displacive behavior of the heavy-ion system.

Crystal Chemistry, Modulated Structure, and Electrical Conductivity in the Oxygen Excess Scheelite-Based Compounds La₁₋ₓThₓNbO₄₊ₓ/₂ and LaNb₁₋ₓWₓO₄₊ₓ/₂. R. J. CAVA,* R. S. ROTH, T. NEGAS, H. S. PARKER, AND D. B. MINOR, Bell Laboratories, Murray Hill, New Jersey 07974. For $La_{1-x}Th_xNbO_{4+x/2}$, three phases with broad homogeneity regions occur, for $0.075 \leq x \leq 0.37$, $0.41 \leq x \leq 0.61$, and $0.65 \leq x \leq 0.74$. All are related to the scheelite structure type, with at least the first exhibiting an incommensurate structural modulation. An analogous structurally modulated phase was found for $LaNb_{1-x}W_xO_{4+x/2}$ for $0.11 \leq x \leq 0.22$. Additional phases occur at $La_{0.2}Th_{0.8}NbO_{4.4}$ and $LaNb_{0.4}W_{0.6}O_{4.3}$. The electrical conductivity and the direction and wavelength of the structural modulation have been characterized for the $La_{1-x}Th_xNbO_{4+x/2}$ phase with $0.075 \leq x \leq 0.37$.

Luminescence Spectra and Raman Excitation Profiles in Small CdS Particles. G. C. PAPAVASSI-LIOU, Theoretical and Physical Chemistry Institute, The National Hellenic Research Foundation, 48, Vas. Constantinou Ave., Athens 501/1, Greece. The "edge"—luminescence spectra and the Raman excitation profiles of small CdS particles chemically deposited on transparent substrates show size effects. The peaks are shifted to higher frequencies as the size of particles decreases. Aggregated samples show maxima at lower frequencies than those of the bulk material and behave as amorphous films. After the samples are warmed, a new peak appears in the luminescence spectra whose position depends on the size and aggregation of the particles. An explanation of the shifts based on the size-quantization of the bandwidth or of the localized electronic levels has been given.

X-Ray Study of the $PbCl_{2-x}I_x$ and $PbBr_{2-x}I_x$ Systems. L. H. BRIXNER,* H.-Y. CHEN, AND C. M. FORIS. Central Research and Development Department, E.I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware, 19898. Compounds from the systems $PbCl_2/PbI_2$ and $PbBr_2/PbI_2$ were examined by X-ray diffraction. The lattice parameters of these phases are presented and the refined crystal structures of the intermediate compounds PbClI and $PbBr_{1.2}I_{0.8}$ are reported. Both structures have *Pbnm* symmetry, are isostructural with $PbCl_2$, and have the different halogens ordered in the two *Cl* sites. Phase studies showed that $PbCl_2$ and PbClI have practically no mutual solubility, while $PbBr_2$ and $PbBr_{1.2}I_{0.8}$ have appreciable solubility ranges, particularly for $PbBr_2$-rich concentrations. At least 17% Br is present in the I site of $PbBr_{1.2}I_{0.8}$. Nevertheless, it is a distinct phase with miscibility gaps toward $PbBr_2$ and PbI_2. This behavior is explained by the size disparity between the halogens. The intermediate phases do not form solid solutions with hexagonal PbI_2.

Mössbauer ^{57}Fe Isomer Shift as a Measure of Valence in Mixed-Valence Iron Sulfides. J. B. GOODENOUGH* AND G. A. FATSEAS, Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, England. An empirical formula relating the room-temperature isomer shift δ for high-spin iron in sulfur coordination to the effective iron valence $\langle m+ \rangle$, of the form $\delta = A - B \langle m+ \rangle$, has been refined for tetrahedral coordination and modified by an inclusion of orbital degeneracy into the definition of $\langle m+ \rangle$; it has also been extended to include octahedral coordination by adding 0.17 mm/sec to A. For a given $\langle m+ \rangle$, the I.S. is shown to be sensitive to nearest-neighbor anion coordination, but much less sensitive than the hyperfine field to the competitive bonding with these anions. However, the sign of the deviation from the empirical line indicates the direction of any net superexchange charge transfer to or from the iron atom. The utility of the relationship is illustrated by application to a wide range of problems.

An Electron Microscope Study of the Rhombohedral Phase Occurring in the Bi_2O_3–BaO System. R. J. D. TILLEY, School of Materials Science, University of Bradford, Bradford, West Yorkshire BD7 1DP, England. The rhombohedral phase which occurs at about 20 mole% BaO in the Bi_2O_3–BaO system has been studied by electron microscopy. While some material seems identical to that found by X-ray diffraction, many crystals show the existence of a superlattice on the electron diffraction patterns. This superlattice is believed to arise as a result of ordering of the Bi and Ba atoms in the structure. Electron micrographs suggest that the ordered regions are small and can be regarded as microdomains within the parent crystal matrix.

On the Relationship between the Structure of $CaFe_2O_4$ and Hollandite. C. M. PLUG, Gorlaeus Laboratories, Rijksuniversiteit, P.O. Box 9502, 2300 RA Leiden, The Netherlands. The relationship between the structure of $CaFe_2O_4$ and those of rutile and hollandite is shown. $CaFe_2O_4$ may be regarded as a glide reflection twin derivative of a distorted hollandite-type structure. On the basis of this structural relationship the possibility of the existence of compounds with intermediate structures is put forward.

Lanthanum β-Alumina Phase Doped with Europium: Optical Investigation by Dye Laser Site-Selective Excitation. J. DEXPERT-GHYS,* M. FAUCHER, AND P. CARO, Laboratoire des Eléments de Transition dans les Solids, 1 Place A. Briand, 92190 Meudon, France. Optical properties of Eu^{3+} doped in (La) β-alumina are studied under conventional ultraviolet excitation and under site-selective excitation using a dye laser. The results are interpreted in terms of structural characteristics: eight different point sites are thus observed for Ln^{3+} (La^{3+} or Eu^{3+}). Following the spectroscopic as well as the previous X-ray diffraction analysis, the mirror plane structure is described as the juxtaposition of microdomains in which Ln^{3+} ions have different immediate environments with 5 to 12 oxygen first neighbors.

An Order–Disorder Transition in Sr_2IrD_5: Evidence for Square Pyramidal IrD_5 Units from Powder Neutron Diffraction Data. J. ZHUANG, J. M. HASTINGS, L. M. CORLISS,* R. BAU, C-Y. WEI, AND R. O. MOYER, JR., Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973. Neutron diffraction data have been collected on a powdered sample of Sr_2IrD_5 over a range of temperatures. The compound, which is cubic at room temperature, has been found to exhibit a gradual transformation to a tetragonal phase in the temperature range 200–140 K. As a result of the transition, deuterium atoms which randomly occupy sixfold positions in the cubic phase, become tetragonally ordered. A small fraction of the cubic phase remained untransformed at 4.2 K. Both the cubic and

tetragonal structures are consistent with square pyramidal IrD_5 units with average Ir–D distances of 1.714 and 1.718 Å, respectively. Agreement factors, R_1, for the two structural analyses are 3.44 and 4.94%.

Heat Capacity of Iron–Chromium Spinels, $Fe_{3-x}Cr_xO_4$. H. INABA,* S. NAKASHIMA, AND K. NAITO, Department of Nuclear Engineering, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan. The heat capacity of $Fe_{3-x}Cr_xO_4$ with the composition $x = 0.6$, 0.8 and 1.0 was measured from 200 to 850 K. A λ-type heat capacity anomaly due to the ferri–paramagnetic transition was observed for all compositions. The transition temperatures were 652, 563, and 451 K for the compositions $x = 0.6$, 0.8, and 1.0, respectively. The variation of transition temperature with composition is discussed in terms of cation distribution. The magnetic contribution to the observed heat capacity was obtained by assuming that the heat capacity is expressed by the sum of the lattice heat capacity $C_v(l)$, the dilation contribution $C(d)$, and the magnetic contribution $C(m)$. Entropy changes due to the transition were calculated from $C(m)$ as 52.6, 49.7, and 46.3 J K^{-1} mole^{-1} for the compositions $x = 0.6$, 0.8, and 1.0, respectively, which are from 7 to 12 J K^{-1} mole^{-1} higher than the calculated values based on the assumption of randomization of unpaired spins on each ion. The difference between the observed and the calculated values is roughly explained by taking into account the orbital contribution of Fe^{2+} ions on octahedral and tetrahedral sites.