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# Abstracts of Forthcoming Articles

*Free Energies of Formation of Metal–TCNQ Anion Radical Salts.* S. ARONSON, AND J. S. MITTELMAN, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, New York 11210. Free energies of formation were determined for the TCNQ anion radical salts of Li, Na, K, Ba, Ag, Cu, Ni, and Pb. Aqueous electrochemical cell measurements at room temperature were used. The results are qualitatively similar to data on the corresponding metal iodides.

*About $SnF_2$ Stannous Fluoride. IV. Kinetics of the $\alpha \rightarrow \gamma$ and $\beta$, $\gamma \rightarrow \alpha$ Transitions.* G. DÉNÈS, Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4M1, Canada. The kinetics of the reconstructive first-order phase transitions $\alpha \rightarrow \gamma$ (upon heating) and $\beta$, $\gamma \rightarrow \alpha$ (upon cooling) of $SnF_2$ were studied by quantitative X-ray powder diffraction. The main feature of the kinetics is that these transformations are incomplete over a wide temperature range. Consequently it is not possible to fit the experimental data using the usual solid-state rate expressions. Although these transitions are not reversible (large hysteresis) the empirical use of a kinetic model of a reversible transformation provides a good fit. The $\alpha \rightarrow \gamma$ transformation was also investigated by D.T.A.; this transition was found to be greatly influenced by particle size: the transition temperature increases with grain size, and its enthalpy decreases. The X-ray investigation revealed that the process of the $\alpha \rightarrow \gamma$ transformation involves an intermediate noncrystalline phase named the "transition phase." It is suggested that the transition proceeds through a process of fragmentation–reconstruction.

*Elastic Strain Energy and Microstructures of Orthorhombic Tin–Tungsten Bronzes.* E. IGUCHI AND R. J. D. TILLEY, School of Materials Science, University of Bradford, Bradford, West Yorks BD7 1DP, U.K. The elastic strain energy of the series of orthorhombic I bronzes which occur in the Sn–W–O system has been calculated using the Fourier transform method. The results of these calculations are compared with microstructures and phase analysis carried out by transmission electron miscroscopy. The two are in good agreement, suggesting that elastic strain energy is important in materials containing planar faults other than crystallographic shear phases.

*Preparation and Mössbauer Studies of $(Fe_yNb_{1-y})_{1+x}S_2$ Compounds.* M. WAKIHARA, H. HINODE, M. ABE, AND M. TANIGUCHI, Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan. The phase relations for iron niobium sulfides $(Fe_yNb_{1-y})_{1+x}S_2$ have been examined by varying the partial pressure of sulfur at 950°C. While niobium is difficult to dissolve in iron sulfide, iron dissolves in niobium sulfide up to about 35% of the total metal sites. Iron niobium sulfide has the layered hexagonal-type structure ($2s$–$Nb_{1+x}S_2$) with change in the lattice parameters depending on both the value of $x$ and the amount of the iron dissolved. The Mössbauer spectra of sulfides with three different Fe/Nb ratios, 1/9 ($y = 1/10$), 1/4 ($y = 1/5$), and 1/2 ($y = 1/3$) were taken at 77 and 295 K. Each spectrum is composed of a quadrupole doublet which can be attributed to the $Fe^{2+}$ ions in a high spin state. The quadrupole splitting at 295 K decreases markedly with a decrease in $x$ which is related to change of the lattice parameters. Fe atoms cannot enter at random into all metal sites, and prefer to intercalate in the sites of partially filled layers. Possible models for the cation distribution in each metal layer are discussed.

*The Crystal Structures of $\alpha$- and $\beta$-$CdUO_4$.* T. YAMASHITA, T. FUJINO, N. MASAKI, AND H. TAGAWA, Division of Chemistry, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-11, Japan. The structural parameters of $\alpha$- and $\beta$-$CdUO_4$ crystals are determined by X-ray powder diffraction technique. $\alpha$-$CdUO_4$ is rhombohedral and its cell parameters are $a = 6.233(3)$ Å and $\alpha = 36.12(5)°$. $\beta$-$CdUO_4$ crystallizes in a C-centered orthorhombic cell with $a = 7.023(4)$, $b = 6.849(3)$, $c = 3.514(2)$Å. The space groups are $R\bar{3}m$ for $\alpha$-$CdUO_4$ and $Cmmm$ for $\beta$-$CdUO_4$. $\alpha$-$CdUO_4$: 1U in (0 0 0), 1Cd in ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$), 2O(1) in $\pm(u\ u\ u)$, 2O(2) in $\pm(v\ v\ v)$; $u = 0.113$, $v = 0.350$, $Z = 1$. $\beta$-$CdUO_4$: 2U in (0 0 0; $\frac{1}{2}$ $\frac{1}{2}$ 0), 2Cd in ($\frac{1}{2}$ 0 $\frac{1}{2}$; 0 $\frac{1}{2}$ $\frac{1}{2}$), 4O(1) in (0, $\pm y$, 0, $\frac{1}{2}$, $\frac{1}{2} \pm y$, 0), 4O(2) in ($\pm x$, 0, $\frac{1}{2}$, $\frac{1}{2} \pm x$, $\frac{1}{2}$, $\frac{1}{2}$); $x = 0.159$, $y = 0.278$, $Z = 2$. $\beta$-$CdUO_4$ contains collinear uranyl $UO_2^{2+}$ groups with the U–O(1) distance 1.91 Å along the $c$ axis, whereas the U–O(1) bond length in $\alpha$-$CdUO_4$ is 1.98 Å which is longer than the usual uranyl bond length.

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*Sensitization of* $Tb^{3+}$ *Luminescence with* $Ce^{3+}$ *in LaOBr:* $Tb^{3+}$, $Ce^{3+}$. J. HÖLSÄ, M. LESKELÄ, AND NIINISTÖ, Department of Chemistry, Helsinki University of Technology, Otaniemi, SF-02150 Espoo 15, Finland. Luminescence emission and uv-excitation properties of LaOBr: $Tb^{3+}$, LaOBr: $Ce^{3+}$, and LaOBr: $Tb^{3+}$, $Ce^{3+}$ phosphors were studied. The visible emission spectra of $La_{0.995}Tb_{0.005}OBr$ consists of ${}^5D_{3,4} \rightarrow {}^7F_{3-6}$ transitions in the wavelength range 410 to 630 nm. The excitation of the $Tb^{3+}$ ion gives a broad $4f \rightarrow 5d$ transition band at 254 nm and weaker $4f \rightarrow 4f$ transition lines above 300 nm. The uv-excitation and emission of $La_{0.995}Ce_{0.005}OBr$ at 290, 315, 355 (excitation), and 440 nm (emission) originate from transitions between the $4f$ ground state and the four crystal field components of the $5d$ ${}^2D$ excited state. The sensitization of $Tb^{3+}$ luminescence in LaOBr with $Ce^{3+}$ at varying concentrations is described and discussed. With increasing $Ce^{3+}$ concentration the ${}^5D_3 \rightarrow {}^7F$ transitions of $Tb^{3+}$ quench totally and the ${}^5D_4 \rightarrow {}^7F$ transitions begin to quench gradually. The excitation spectrum of the ${}^5D_4 \rightarrow {}^7F_5$ transition of $Tb^{3+}$ consists of four bands due to $Tb^{3+}$ and $Ce^{3+}$, of which the three $Ce^{3+}$ bands increase in intensity and the $Tb^{3+}$ band decreases as the $Ce^{3+}$ concentration is increased.

*The Crystal Structure of 3-R* $Nb_{108}S_2$. D. R. POWELL AND R. A. JACOBSON, Ames Laboratory, Department of Chemistry, Iowa State University, Ames, Iowa 50011. The X-ray single-crystal structure of 3-R $Nb_{1.08}S_2$ has been determined. The material crystallizes in the space group $R3m$ with $a$ =3.3285(4) Å and $c$ = 17.910(4) Å when indexed on a hexagonal lattice. The structure was refined by full-matrix least-squares procedures to a final residual of $R = 0.026$ based on 79 observed ($I > 3\sigma_I$) reflections. The sulfurs form closest-packed layers with the majority of the metal in sheets of trigonal prismatic sites. A small portion of niobium was found to occupy octahedral sites, between the van der Waals gaps of the sulfur lattice. Niobium in the van der Waals region is trigonally distorted from octahedral symmetry, with niobium–sulfur distances of 2.234(8) and 2.577(11) Å, because of repulsion from niobium in adjacent trigonal prismatic layers.

*Solid State Reactions in Chalcogenide Systems. VI. Ion Distribution Equilibria between* $MCr_2(S, Se)_4$ *Spinel Solid Solutions and* $M(S, Se)$ *or* $Cr_2(S, Se)_3$ *Solid Solutions.* H. D. LUTZ, W. BECKER, AND W. W. BERTRAM, Laboratorium für anorganische Chemie der Universität Siegen. D 5900 Siegen 21, Germany. The sulfur/selenium exchange equilibria between spinel solid solutions $MCr_2(S, Se)_4$ ($M$ = Zn and Cd) and $M$(S, Se) or $Cr_2(S, Se)_3$ solid solutions with sphalerite, wurtzite, and defect NiAs structure have been determined by X-ray diffraction measurements of reaction mixtures quenched from 1073 and 1273 K, respectively. With the exception of the $CdCr_2X_4/Cr_2X_3$ system, there is a clear preference for incorporation of sulfur in the spinel structure, increasing in the series $ZnCr_2X_4/Cr_2X_3 < ZnCr_2X_4/ZnX < CdCr_2X_4/CdX$. Both equilibrium constants and reaction heats, including data on $MCr_2S_4/M'S$ ($M, M'$ = Mn, Co, Zn, and Cd) metal ion distribution equilibria, are given. Revised X-ray data on the solid solutions are also presented.

*Etude du comportement du niobium(IV) et du titane(III) dans quelques oxydes à structure en cages du types* $A_3M_8O_{21}$. *I. Synthèse et evolution structurale des solutions solides* $Ba_3Nb_{4-x}Ti_{4+x}O_{21}$, $K_3Nb_{7+x}Ti_{1-x}O_{21}$, *et* $K_{3-x}Ba_xNb_8O_{21}$. J. M. CHAILLEUX, D. GROULT, C. MERCEY, F. STUDER, AND B. RAVEAU, Groupe de Cristallographie et Chimie du Solide, ISMRA-Université de Caen, 14032 Caen Cédex, France. New solid solutions $A_3Nb_{8-x}Ti_xO_{21}$ (A = K, Ba) and $K_{3-x}Ba_xNb_8O_{21}$ have been synthesized. They crystallize in the hexagonal $A_3M_8O_{21}$ structure. In the series $Ba_3Nb_{4+x}Ti_{4-x}O_{21}$ ($0 \leq x \leq 1$) the break in the evolution of the lattice constants observed respectively for $x$ =2 for the former and $x = 0.5$ for the latter has been interpreted as the result of the reaction Nb(IV) + Ti(IV) → Nb(V) + Ti(III). The better stability for the combination Nb(V)/Ti(III) in the host lattice is confirmed by the estimation of the energy levels in the structure which takes into consideration the ionization and the polarization energies.

*Calculation of Polarization Energies in Some III–VII and IV–VI Compounds with Stereochemically Active* $(ns)^2$ *Ions.* C. P. J. M. VANDER VORST AND J. A. J. BASTEN, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, The Netherlands. The polarization energies of $AB$ compounds, with $A$ a monovalent or divalent cation with an $(ns)^2$ lone pair and $B$ an anion with a noble gas electronic configuration, have been calculated to investigate whether the stereochemical activity of the $(ns)^2$ ion can be understood in an ionic picture. Computations have been performed applying the computer program EWALD. Formal ionic charges and partly estimated polarizabilities have been used. The polarization energy is shown to be predominantly due to cation polarization and may constitute an appreciable fraction of the total lattice energy. Hence, it can play a crucial role in the formation of structures, in which the $(ns)^2$ ion is in a noncentrosymmetrical environment.

*Thermopower Composition Dependence in Ferrospinels.* C. C. WU, S. KUMARAKRISHNAN, AND T. O. MASON, Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60201. The composition dependence of thermoelectric power (Seebeck coefficient) in ferrospinels with fixed-valence foreign cations has been calculated via combined small polaron and cation distribution models. Satisfactory agreement with experimental data is achieved assuming cation distribution thermodynamic constants to be independent of foreign cation concentration. Data are analyzed for a trivalent foreign cation ($Al^{3+}$) at elevated temperature and for divalent foreign cations ($Ni^{2+}$, $Mg^{2+}$, $Zn^{2+}$) at lower temperatures.

*The Boron–Silicon Solid Solution: A Structural Study of the $SiB_{\sim 36}$ Composition.* M. VLASSE AND J. C. VIALA, Laboratoire de Chimie du Solide, Université de Brodeaux I, 351 cours de la Libération, 33405 Talence Cédex, France. The structure of a crystal of a solid solution of silicon in $\beta$-rhombohedral boron has been studied by single-crystal X-ray diffractometry. The final $R$ value was 5.4% for 815 reflections. The space groups is $R\bar{3}m$ and hexagonal lattice parameters are $a = 11.01(1)$ Å, $c = 23.90(2)$ Å. The cell contains 305.51 boron and 8.443 silicon atoms. The boron framework of $\alpha$-boron is only slightly changed. Two Si atoms occupy interstitial holes. A third silicon substitutes partially for a framework boron atom. The results obtained are discussed.

*A Series of Oxygen-Defect Perovskites Containing $Cu^{II}$ and $Cu^{III}$: The Oxides $La_{3-x}Ln_xBa_3[Cu^{II}_{5-2y}Cu^{III}_{1+2y}]O_{14+y}$.* L. ER-RAKHO, C. MICHEL, J. PROVOST, AND B. RAVEAU, Laboratoire de Cristallographie et Chimie du Solide, Institut des Sciences de la Matière et du Rayonnement, Université de Caen, Esplanade de la Paix, 14032 Caen Cédex, France. A series of oxygen-defect perovskites, containing $Cu^{II}$ and $Cu^{III}$, $La_3B_3[Cu^{II}_{5-2y}Cu^{III}_{1+2y}]O_{14+y}$, has been synthesized at 1000°C, for $0 \cdot 05 \leq y \leq 0 \cdot 43$. The substitution of lanthanum for yttrium and lanthanides has been studied. These oxides are tetragonal: $a = a_p 2^{1/2}$ and $c = 3a_p$. The structural study of $La_3Ba_3Cu_6O_{14.10}$ shows that oxygen vacancies are ordered, involving for copper three sorts of coordination: square, pyramidal (4 + 1), and distorted octahedral (4 + 2). The distribution of $Cu^{III}$, as well as the lanthanide ions on the different sites, is discussed.

*Neutron Powder Diffraction and Magnetic Measurements on $TlMnI_3$ and $TlFeI_3$.* H. W. ZANDBERGEN, Gorlaeus Laboratories, University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands. $TlMnI_3$ and $TlFeI_3$ are isostructural with $NH_4CdCl_3$. $TlMnI_3$ has a spiral structure which can be described with an incommensurable vector **k**, in the direction of the $b^*$ axis of length $0.361(5)b^*$. The spin lies in the (0 0 1) plane. $TlMnI_3$ exhibits antiferromagnetic behaviour with a Néel temperature of 6.0(2) K. The exchange interaction was calculated to be $zJ/K = -1.6$ K, $z$ being the number of the nearest neighbors. Discontinuities in the magnetization are found for both the [1 0 0] and [0 1 0] directions at fields $H^a_{SF} = 30.1(2)$ kOe and $H^b_{SF} = 14.1(2)$ kOe. The magnetic structure of $TlFeI_3$ consists of puckered ferromagnetic (1 0 0) planes, which are coupled antiferromagnetically. The magnetic moments are parallel to the $b$ axis. The Néel temperature is 21.5(3) K. $zJ/k$ was found to be 10.(1) K with $g = 2.68$ and $s = 2$. The magnetic structures found for $TlMnI_3$ and $TlFeI_3$ are derived taking into account inter- and intra- double-chain interactions via two $I^-$ ions.

*Some Systematics of the Garnet Structure.* F. C. HAWTHORNE, Department of Earth Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada. Equations relating the positional parameters of the anion in the oxide garnets to the mean constituent ionic radii of the cations occupying the $\{X\}$, $[Y]$, $(Z)$ sites have been derived from published garnet structures using multiple regression analysis: $x = 0.0278(22)r\ \{X\} + 0.0123(28)r\ [Y] - 0.0482(16)r(Z) + 0.0141$; $y = -0.237(25)r\ \{X\} + 0.0200(32)r\ [Y] + 0.0321(18)r(Z) + 0.0523$; $z = -0.0102(20)r\ \{X\} + 0.0305(25)r\ [Y] - 0.0217(14)r(Z) + 0.6519$. Variations of mean bond lengths with constituent ionic radius are examined for the garnet structures. Deviations of mean bond length from the sum of the constituent ionic radii may be correlated with the ionic radius of the cations at the other sites in the structure.

*The Crystal Structure of a New Mixed Oxide of Iron and Vanadium, $(Fe, V)_{18}O_{35}$.* I. E. GREY, M. ANNE, A. COLLOMB, J. MULLER, AND M. MAREZIO 166X, 38042 Grenoble Cédex, France. Single crystals of a new compound, $Fe_{6.5}V_{11.5}O_{35}$ have been prepared by hydrothermal synthesis at 650°C and

2 kbar. The compound has triclinic symmetry, $P\bar{1}$, $Z = 1$, with unit cell dimensions $a$ = 10.209(3) Å, $b$ = 9.387(3) Å, $c$ = 6.564(2) Å, $\alpha$ = 100.52(5)°, $\beta$ = 94.35(5)°, $\gamma$ = 98.85(4)°. It structure was determined using direct methods and refined to an $R$ value of 0.053 ($wR$ = 0.038) for 5654 observed reflections ($F > 3\sigma(F)$) whose intensities were measured on a Philips PW1100 diffractometer using Ag$K\alpha$ radiation. The structure is based on a cubic close-packed framework of anions in which cations are ordered into tetrahedral ($V^{5+}$), square pyramidal ($V^{4+}$), and octahedral ($Fe^{3+}$, $V^{4+,3+}$) sites. The structure comprises zigzag chains of eight edge-shared octahedra ($\alpha$-$PbO_2$-like) which are crosslinked via corner sharing with tetrahedra and square pyramids, and via edge sharing with square pyramids and octahedra. Bond length–bond strength considerations were used to establish the cation valence-state assignments and the different sites, giving a unit cell composition $Fe^{3+}_{6.5}V^{3+}_{1.5}V^{4+}_{4}V^{5+}_{6}O_{35}$.

*The Influence of Cation Arrangement on the EPR Spectrum of* $Mn^{2+}$ *in the Spinel Compounds* $CdB_2X_4$. L. PAWLAK, K. FALOWSKI, AND S. POKRZYWNICKI, Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University, 50-370 Wroclaw, Poland. $CdB_2X_4$ spinels ($B$ = Sc, Y, Lu; $X$ = S, Se) were synthesized and their lattice constants were determined. After $Mn^{2+}$ doping they were investigated by the EPR method over the temperature range 4.2 to 330 K. The temperature dependence of hyperfine-structure constant $A$ was described by the Šimanek–Orbach equation and its parameters were determined. Chemical bonds in the studied spinels were characterized in more detail to obtain a linear dependence of the $A$ constants on the modified covalency parameter.

*Chemical Diffusion in Intermediate Phases in the Lithium–Silicon System.* C. JOHN WEN AND R. A. HUGGINS, Department of Materials Science and Engineering, Stanford University, Stanford, California 94305. The equilibrium coulometric titration curve shows four intermediate phases in the Li–Si system at 415°C. The nominal compositions for these phases are $Li_{12}Si_7$, $Li_7Si_3$, $Li_{13}Si_4$, and $Li_{22}Si_5$, respectively. They all have quite narrow ranges of homogeneity. The compositional variations of the chemical diffusion coefficients within the various intermediate phases are similar to each other and closely resemble those of the thermodynamic enhancement factor for each phase. The chemical diffusion coefficients across all four intermediate phases are essentially of the same order, about $6.0 \times 10^{-5}$ cm²/sec at 415°C.

*Zeolite Structure Type EAB; Crystal Structure and Mechanism for the Topotactic Transformation of the Na, TMA Form.* W. M. MEIER AND M. GRONER, Institut für Kristallographie und Petrographie, ETH, Zurich, Switzerland. Synthetic zeolite (Na, TMA)-E represents a new structure type designated EAB. Detailed structure analyses based on X-ray powder diffraction data have been carried out at room temperature, 220°C, and 350°C. The silicate framework, having maximum symmetry $P6_3/mmc$, consists of parallel 6-rings in *ABBACC* sequence as opposed to *AABAAC* in erionite (with which it has mistakenly been identified). Large changes in conformation of the EAB framework precede the transformation of (Na, TMA)-E to sodalite type product above 360°C. There are also strong indications for this reaction to be topotactic whereby only 1/12 of the original siloxane bridges are broken. Details of an acid–base reaction mechanism proceeding in characteristic loops of the structure are discussed. This process brings about the inversion of one-third of the tetrahedra in the silicate framework. The presence of water appears to be essential in this model-type reaction.

*An Electron Microscope Examination of* $VF_2$. H. A. EICK AND L. EYRING, Department of Chemistry, Arizona State University, Tempe, Arizona 85281. Samples of blue and black $VF_2$, the latter prepared by heating blue $VF_2$ with $VF_3$ in a sealed crucible, were examined in the electron miscroscope. A nonintegral superstructure pattern was observed. Evidence presented supports the hypothesis that this superstructure results from the epitaxial growth of a phase, possibly an oxide, on the surface of the black $VF_2$ and upon that of both the blue and black forms of $VF_2$ in a twinned mode upon electron beam irradiation. The capability of the miscroscope to facilitate explanation of these unexpected results is discussed.

*Defect Structures in the Brannerite-Type Vandates. III. Preparation and Study of* $Cu^{2+}_{1-x-y}Cu^{1+}_{y}\phi_x V_{2-2x-y}Mo_{2x+y}O_6$ ($x_{\max} = 0.23$; $y_{\max} = 0.27$). T. MACHEJ, R. KOZLOWSKI, AND J. ZIOLKOWSKI, Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek, 30-239 Kraków, Poland. Phases of the formula $Cu^{2+}_{1-x-y}Cu^{1+}_{y}\phi_x V_{2-2x-y}Mo_{2x+y}O_6$, where $\phi_x$ represents a vacancy at $Cu^{2+}$ site, have been synthesized and characterized by X-ray diffraction, DTA, and magnetic susceptibility measurements. The extent of their homogeneity range has been established. All crystallize in the structure closely related to the brannerite type with the symmetry reduced from monoclinic to triclinic because of a Jahn–Teller distortion of $CuO_6$ octahedra. On heating they undergo a phase transformation to a monoclinic phase. Unit cell dimensions and transition temperatures were compiled for eight samples of the solid solution, and correlations were established between the chemical composition ($x$, $y$) and structural parameters. Changes in unit cell parameters involve the expansion of the lattice and the systematic evolution of the triclinic unit cell to the monoclinic one.

*The Position of Yttrium within Lanthanides in Respect to Unit Cell Volumes of Isostructural Compounds as an Indication of Covalency in Lanthanide Compounds.* S. Siekierski, Department of Radiochemistry, Institute of Nuclear Research, Warsaw 03-195, Poland. The position of yttrium in the lanthanide series in respect to unit cell volumes has been determined from literature data for 52 isostructural $M_mX_n$ compounds of lanthanides and yttrium. A linear correlation between the position and the electronegativity of $X$ atom has been demonstrated. This result has been explained in terms of covalent shortening of the $M$–$X$ bonds in lanthanide compounds.

*Stability Relations in the Pseudobrookite Solid Solutions* $Fe_yTi_{3-y}O_5$. I. E. Grey and R. R. Merritt, CSIRO Division of Mineral Chemistry, P.O. Box 124, Port Melbourne, Victoria 3207, Australia. The stability relations in the pseudobrookite solid solution $Fe_yTi_{3-y}O_5$ have been studied in the temperature range 1350–1623°K, using the quench method and controlled gaseous buffers. The temperature/oxygen-fugacity relationships for three univariant assemblages containing the pseudobrookite solid solution have been established, and the composition/temperature curve delineating the pseudobrookite solid solution and its decomposition products has been defined. This curve exhibits two maxima at temperatures of 1413 and 1619°K and corresponding compositions of $FeTi_2O_5$ and $Fe_{0.30}Ti_{2.70}O_5$. The intervening minimum occurs at a temperature of 1339°K and a composition of $Fe_{0.9}Ti_{2.1}O_5$. A qualitative explanation for the shape of the stability curve is given in terms of the relative contributions to the free energy from configurational entropy and enthalpy (internal strain).

*Phase Equilibria and Compound Formation in the Nd–Mo–O System between 1273 and 1673°K.* H. Czeskleba-Kerner, B. Cros, and G. Tourné, Laboratoire de Chimie des Solides, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 Montpellier Cédex, France. Phase equilibria in the $Nd_2O_3$–$MoO_2$–$MoO_3$ system have been investigated at 1273, 1473, and 1673°K under controlled gaseous atmosphere with emphasis on the formation and stability of ternary phases. New fluorite-related compounds of molybdenum (VI) and (V) have been characterized: $Nd_6MoO_{12}$, $Nd_{10}Mo_2O_{21}$, and $Nd_3MoO_7$. In the $MoO_2$-rich portion of the phase diagram a new cubic related molybdenum (IV) compound, $Nd_2Mo_3O_9$, has been found. On the basis of phase equilibria at 1473°K, the standard free energy of formation of $Nd_2MoO_5$, $Nd_3MoO_7$, $Nd_6MoO_{12}$, and $Nd_2MoO_6$ was determined from metallic molybdenum, $Nd_2O_3$, and oxygen. The role of the rare earth element in selective oxidation of molybdenum and crystal chemical properties of the ternary compounds are discussed in relationship to the neighboring systems of praseodymium and samarium oxides.

*Phase Transitions in* $CsH_2AsO_4$ *at High Pressures and Temperatures.* S. Hart, P. W. Richter, J. B. Clark, and E. Rapoport, National Physical Research Laboratory, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria 0001, South Africa. $CsH_2AsO_4$ (CDA) is an analogue of the well-known ferroelectric $KH_2PO_4$ (KPD). The phase diagram of CDA has been established to the melting curve and up to 4 GPa. Evidence for three new phases has been found.

*Investigation of Composition and Chemical State of Elements in Iron Boride by Method of X-Ray Photoelectron Spectroscopy.* V. G. Alyoshin, A. I Kharlamov, and V. M. Prokopenko, Institute of Metal Physics, Academy of Sciences of Ukr.SSR, Kiev, Ukr.SSR. The composition and chemical state of iron and boron in the surface layer of iron boride under different kinds of pretreatment of samples have been investigated by the method of X-ray photoelectron spectroscopy. It has been found that in the initial sample there is oxygen chemically combined with iron and boron atoms. Upon heating (450°C) in hydrogen, argon, and *in vacuo* there occurs removal of oxygen only from iron atoms (no pure iron was found to be formed). Boron oxidizes and there, probably, appears a new surface combination of boron with oxygen in which the bonding energy of 1*s* electrons is higher than in $B_2O_3$. Treatment of the iron boride surface with argon ions and with protons ensures uniform removal of oxygen from iron and boron atoms. It has been found that thermal treatment of iron boride leads to impoverishment of the sample surface layer of iron atoms, and pickling with argon ions and with protons leads to strong enrichment. Iron boride samples subjected to $Ar^+$ and $H^+$ bombardment tend to undergo significant oxidation when subsequently exposed to air at room temperature.

*Recherche de Matériaux á conductivité ionique ameliorée derivant des hydrurofluorures de calcium* $CaF_{2-x}H_x$*: Conductivité ionique des phases* $Ca_{1-y}Na_y(F_{2-x}H_x)_{1-y/2}$. J. F. BRICE, R. LEVEQUE, AND P. STEINMETZ, Laboratoire de Chimie du Solide Mineral, Université de Nancy I, C.O. 140, 54037 Nancy Cédex, France. The doping of $CaF_{2-x}H_x$ hydridefluorides by aliovalent ions is studied, the aim being the preparation of materials of improved ionic conductivity. It is shown that doping by monovalent $Na^+$ ions is possible. Three hydrogen-rich phases, formulated $Na_yCa_{1-y}(F_{2-x}H)_{1-y/2}$, have been studied. Their conductivity is mainly ionic, but, compared with the same doping in $CaF_2$, the conductivity enhancement is low. This result is interpreted from energetic and structural considerations.

*Neutron Powder Diffraction and Magnetic Measurements on* $RbTiI_3$*,* $RbVI_3$*, and* $CsVI_3$. H. W. ZANDVBERGEN, Gorlaeus Laboratories, University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands. $CsVI_3$ ($a$ = 0.124(1) Å, $c$ = 6.774(1) Å, $Z$ = 2,$P6_3/mmc$ at 293 K) adopts the $BaNiO_3$ structure. Three-dimensional magnetic ordering takes place at $T_c$ = 32(1) K. At 1.2 K the magnetic moment is 1.64(5) $\mu_B$ and it forms a 120° spin structure in the basal plane. $RbVI_3$ ($a$ = 13.863(2) Å, $c$ = 6.807(1) Å, $Z$ = 6,$P6_3cm$ or $P\bar{3}c1$ at 293 K) and $RbTiI_3$ ($a$ = 14.024(3) Å, $c$ = 6.796(2) Å, $Z$ = 6,$P6_3cm$ or $P\bar{3}c1$ at 392 K) adopt a distorted $BaNiO_3$ structure, probably isostructural with $KNiCl_3$, $T_c$ of $RbVI_3$ is 25(1) K. At 1.2 K, $RbVI_3$ has a spin structure similar to the one of $CsVI_3$ with a magnetic moment of 1.44(6) $\mu_B$. $RbTiI_3$ shows no magnetic ordering at 4.2 K. It is shown that a deviation from the 120° structure is expected for compounds with a distorted $BaNiO_3$ structure such as $RbVI_3$. The cell dimensions of $CsTiI_3$ are reported.

*The Resistivity and Magnetic Susceptibility of* $V_3O_5$ *Single Crystals.* H. JHANS AND J. M. HONIG, Department of Chemistry, Purdue University, West Lafayette, Indiana, 47907. New resistivity studies on single-crystal $V_3O_5$ show that the phase transformation at 427 K involves an insulator–metal transition: the resistivities reported here lie somewhat below those cited in numerous earlier investigations. Magnetic susceptibility ($\chi$) measurements exhibit only very small changes at the transition. It is pointed out that the maximum in $\chi$ at 125 K should be correlated with the onset of antiferromagnetic ordering near 76 K.

*Forces de la liaison Te–O: Coordination et localisation de la paire libre de l'atome de tellure (IV) dans les tellurites.* E. PHILIPPOT, Laboratoire de Chimie Minérale C, ERA 314, Chimie des Matériaux, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 Montpellier Cédex, France. The calculation of bond valences ($S$) from the bond lengths ($R$) observed in many accurate structure determinations of tellurites, $Te^{IV}$, using the relations $S = S_0(R/R_0)^{-N}$ allows us to refine the $R_0$ and $N$ values proposed by Brown. If we classify the different $TeO_y$ surroundings by taking into account the three strongest bond valences in their relation to the weakest ones, it can be verified that the observed variation allows us to foresee the atomic coordination of the tellurium (IV) atom with respect to the other components of the structure. On the other hand, the probable location of the lone pair $5s^2$ of the tellurium (IV) atom can be related to the evolution of its coordination.