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Abstracts of Forthcoming Articles

Electronic Structure and Properties of NbS_3 and Nb_3S_4. D. W. BULLETT. Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE United Kingdom. Electronic structure calculations for NbS_3 and Nb_3S_4 are reported. The NbS_3 structure is closely related to that of $ZrSe_3$. In the undistorted $ZrSe_3$ atomic arrangement, NbS_3 would be a metal; it is shown that the observed distortion, a pairing of Nb atoms along the b-axis relative to $ZrSe_3$, stabilizes the NbS_3 crystal by inducing a 0.5-eV semiconducting gap. Nb_3S_4 is found to be a metal with the Fermi level lying near a deep minimum in the density of electron states.

Le Systeme Ga–Se et les Seleniures de Gallium. R. OLLITRAULT-FICHET, J. RIVET, AND J. FLAHAUT. Laboratoire de Chimie Minérale et Structurale Faculte des Sciences Pharmaceutiques et Biologiques de l'Universite Rene Descartes, 4, avenue de l'Observatoire, 75270 Paris Cedex 06, France. New description of the phase diagram. The observed phases are: GaSe, which has several polytypic forms, and Ga_2Se_3 which has two varieties: the first one, cubic of the blende type ($a = 5.454$Å) is stable at high temperature; the second one, monoclinic Bb, is a superstructure of a "tetragonal blende", and is stable at low temperature. Between these two varieties exists an order–disorder transition at 730°C. A third form of Ga_2Se_3, a "distorted blende," is a "blende" in which no superstructure is observed, and which is stabilized by layer defects; it is formed, during the cooling, at 730°C. It is not a thermodynamic stable variety and it cannot be present in the equilibrium phase diagram. But it is the usually observed form of Ga_2Se_3. It gives a solid solution on the Se-rich side of Ga_2Se_3 up to the composition $GaSe_{1.95}$, for which a peritectic is observed at 880°C. A liquid–liquid phase separation is present in the Se-rich part of the diagram.

X-Ray Photoelectron Spectra of 3d-Transition Metal Pyrites. H. VAN DER HEIDE, R. HEMMEL, C. F. VAN BRUGGEN, AND C. HAAS. Laboratory of Inorganic Chemistry, Materials Science Center of the University, Nijenborgh 16, 9747 AG Groningen, The Netherlands. Photoelectron spectra of the synthetic compounds FeS_2, CoS_2, NiS_2, $MnSe_2$, $CoSe_2$, and $NiSe_2$ and of a natural crystal of MnS_2, all with the pyrite structure, are reported. The sulfur $3s$ and selenium $4s$ contributions are split into peaks for bonding and antibonding orbitals due to the covalent bonding in the molecular anion pairs. The difference in lineshape of the peaks for the bonding and antibonding orbitals is attributed to vibronic effects. The metal $2p_{3/2}$ spectra show the effects of multiplet splitting and satellites due to shake-up or shake-off processes. The valence band spectra consist of slightly overlapping contributions of anion p and metal $3d$ electrons. The metal $3d$ spectrum of FeS_2 has a single strong peak of width 0.9 eV. The $3d$ spectra of the other compounds show structure due to several final-state configurations.

Silicates Synthétiques à Structure Milarite. NINH NGUYEN, JACQUES CHOISNET, AND BERNARD RAVEAU. Laboratoire de Cristallographie et Chimie du Solide, L.A. 251 ISMRA Université, 14032 Caen Cedex, France. Twelve new silicates with a milarite-type structure were synthesized. Their general formula is $A_xM_3M'_2Si_{12}O_{30}$. M sites show a tetrahedral coordination (M = Mg, Zn, Fe^{II}, Cu^{II}, Li) and M' sites an octahedral coordination (M' = Mg, Cu^{II}, Fe^{II}). The A elements, with a larger size (Na, K, Rb), occupy two types of sites formed by the host lattice: twelve coordinated sites in the tunnels bounded by the $Si_{12}O_{30}$ rings and nine coordinated sites between these rings. The latter site is half occupied for $x = 2$ and fully occupied for $x = 3$. The tetrahedral coordination of Cu^{II}, as evidenced by X-ray structural determination and infrared spectrometry, is of particular interest. In milarite-type silicates, Cu^{II} exhibits a site preferency for a flattened tetrahedral coordination.

The Luminescence of Pr^{3+} in $BaY_4Si_5O_{17}$. J. TH. W. DE HAIR. Philips Lighting Division, Eindhoven, The Netherlands. The cell constants of four new monoclinic compounds $BaR_4X_5O_{17}$ (R = Y, Gd; X = Si, Ge) are given. The luminescence of various RE activators in the silicates is reported. Pr^{3+}-Activated

$BaY_4Si_5O_{17}$ shows efficient ultraviolet $5d \rightarrow 4f$ emission and weak $4f \rightarrow 4f$ emission (mainly red luminescence from the $^1D_2$ level). The $5d \rightarrow 4f$ emission is ascribed to Pr^{3+} on Y sites, the $4f \rightarrow 4f$ emission to Pr^{3+} on Ba sites. Energy transfer from Pr^{3+} to Gd^{3+} has been observed. Gd^{3+} plays an intermediate role in the energy transfer from Pr^{3+} to Sm^{3+} and to Dy^{3+} in $BaGd_4Si_5O_{17}$. Upon activation with Tb^{3+} the silicates show characteristic green Tb^{3+} luminescence with a quantum efficiency of 75% for ultraviolet excitation.

Synthesis and Electrical Properties of New Chalcogenide Compounds Containing Mixed (Mo, Me)$_6$ Octahedral Clusters (Me = Ru or Rh). A. PERRIN, R. CHEVREL, M. SERGENT, AND Ø. FISCHER. Université de Rennes-Beaulieu, Laboratoire de Chimie Minérale B, Avenue du Général Leclerc, 35042 Rennes Cédex, France. We report the synthesis and some properties of new compounds and some solid solutions containing mixed octahedral $(Me)_6$ clusters (Me = Mo, Ru, Rh). The compound $Mo_4Ru_2Se_8$ is semiconducting whereas the limit compounds $Mo_4Ru_2Te_8$ and $Mo_{4.66}Rh_{1.33}Te_8$ are metallic. Superconductivity was found around the composition Mo_5RuTe_8.

Two New Long-Period Structures Related to β-Alumina. JAN-OLOV BOVIN AND M. O'KEEFFE. Department of Chemistry, Arizona State University, Tempe, Arizona 85281. Two new ordered forms of "β-alumina" with rhombohedral symmetry have been discovered and their structures deduced from one-dimensional electron microscope images of thick crystals. Referred to a hexagonal cell, their lattice parameters are $a = 5.59$ Å, $c = 169.5$ Å and $a = 5.59$ Å, $c = 339$ Å. A symbolism for describing structures related to that of β-alumina is proposed.

Free Energy of Formation of PdO by Impedance Dispersion Analysis. H. J. DE BRUIN AND S. P. S. BADWAL. School of Physical Sciences, The Flinders University of South Australia, Bedford Park, South Australia 5042, Australia. The sharp increase in low-frequency impedance at a Pd/solid electrolyte interface below the thermodynamic transition temperature has been used to determine the free energy of formation for PdO. This observation has been exploited in the development of a new generation of absolute oxygen monitors.

One-Dimensional Condensation of Octahedral Clusters Mo_6: A New Cluster Mo_{12} and a New Building Block $Mo_{12}S_{14}$ in $M_2Mo_9S_{11}$. R. CHEVREL, M. POTEL, M. SERGENT, M. DECROUX, AND Ø. FISCHER. Université de Rennes, Laboratoire de Chimie Minérale B, Avenue du Général Leclerc, 35042 Rennes Cedex, France. Two new Mo compounds, $Tl_2Mo_9S_{11}$ and $K_2Mo_9S_{11}$, have been found. The structure of these compounds is characterized by the presence of a completely new building block, $Mo_{12}S_{14}$, in addition to the well-known Mo_6S_8 unit as in the $PbMo_6S_8$-type compounds. The new cluster Mo_{12} contained in the $Mo_{12}S_{14}$ unit can be considered as a one-dimensional condensation of three Mo_6 octahedral clusters. These new materials, whose structure resembles that of $PbMo_6S_8$, are metallic but are not superconducting above 2.1°K.

The Factors Influencing Coordination Numbers in Solids. JEREMY K. BURDETT AND GUY L. ROSENTHAL. Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. An empirical plot of average principal quantum number ($\bar{n}$) versus average AX electronegativity difference ($\Delta\chi$) for A_nX_m structures shows resolution of four-, six-, and eight-coordinate solid-state structures (Pearson diagrams). A simple molecular orbital (and therefore covalent) analysis of the coordination number problem suggests that it is determined by the balance between X–X nonbonded repulsions and the number of stabilizing interactions (both of which increase with coordination number). A-A repulsions may also be important if A is significantly larger than X. The approach provides an alternative to the ionic model for structure rationalization but it is still not clear how relatively important covalent and ionic factors are in determining the structures of even "ionic" solids.

Structural Studies by X-Ray Diffraction and Mössbauer Spectroscopy of Cubic $FeYb_2S_4$ and $FeLu_2S_4$. A. TOMAS, L. BROSSARD AND M. GUITTARD. Laboratoire de physique, Faculté des Sciences Pharmaceutiques et Biologiques, 4, avenue de l'Observatoire, 75270 Paris Cedex 06, France. The two isostructural compounds $FeYb_2S_4$ and $FeLu_2S_4$ were studied by X-ray diffraction and Mössbauer spectroscopy. The structure was solved in the space group $Fd3m$; $Z = 8$. For $FeYb_2S_4$, the S atoms occupy the ($32e$) positions. The tetrahedral ($8a$) and octahedral ($16d$) positions of the direct spinel are respectively occupied by $0.8Fe^{2+}$ and ($0.88Yb^{3+} + 0.045\ Fe^{2+}$). The additional octahedral ($16c$) positions are occupied by ($0.12Yb^{3+} + 0.55Fe^{2+}$). For 155 reflections crystallographic R is 0.034. The Mössbauer spectrum results from the superposition of four doublets. Two doublets with the same isomer shift $\delta = 0.73$ mm/sec are characteristic of Fe^{2+} ions in ($8a$) position with two distorted tetrahedral symmetries simulated by two different quadrupole splittings. The third and fourth doublets correspond to Fe^{2+} ion in $16c$ and $16d$ positions. The intensity ratio between the doublets is in agreement with the following distribution $(Fe_{0.8}{}^{2+}\square_{0.2})\ (Yb_{1.76}{}^{3+}Fe_{0.09}{}^{2+}\square_{0.15})(Yb_{0.24}{}^{3+}Fe_{0.11}{}^{2+}\square_{1.65})S_4$ which corresponds to $FeYb_2S_4$. The metal atoms in $FeLu_2S_4$ are distributed in the same way as in $FeYb_2S_4$.

Subsolidus Equilibria in the System $BaO–TiO_2–Al_2O_3$. J. P. GUHA. Institute Josef-Stefan, University of Ljubljana, Jamova 39, 61000 Ljubljana, Yugoslavia. The subsolidus phase equilibrium relations in the system $BaO–TiO_2–Al_2O_3$ have been investigated using conventional solid-state reaction techniques and X-ray powder diffraction. The existence of three known ternary compounds, $BaTi_5Al_2O_{14}$, $BaTiAl_6O_{12}$, and $Ba_3TiAl_{10}O_{20}$, was confirmed and their stability relations studied. Various tie lines existing between the ternary compounds and the binary titanates and aluminates of barium were established and a subsolidus phase diagram showing the phase assemblages compatible at 1200°C is presented.

The Crystal Structure of Li_2WO_4IV, and Its Relation to the Wolframite-Type Structure. HIROYUKI HORIUCHI, NOBUO MORIMOTO, AND SHINOBU YAMAOKA. The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan. Li_2WO_4IV, the densest phase among four polymorphs crystallizes with monoclinic symmetry, $C2/c$, $a = 9.753(1)$, $b = 5.954(1)$, $c = 4.994(1)$ Å; $\beta = 90.58(2)°$; $Z = 4$; $D_{calc} = 6.00\ g\ cm^{-3}$. The structure was determined by counter-measured 1765 independent reflections with a single crystal synthesized at 40 kbar and 850°C and refined to $R = 0.067$ by the full-matrix least-squares method. It is based on a hexagonal closest arrangement of oxygen atoms and is structurally closely related to the wolframite-type structure. Both the tungsten and the lithium atoms are in octahedral sites. The structure consists of four octahedral layers parallel to (100). The first and the third layers are filled by lithium atoms, resulting in LiO_6 octahedral sheets, while the second and the fourth contain zig-zag chains of WO_6 octahedra observed in the wolframite structure.

Structural and Physical Properties of $Cr_{3\pm x}Se_4 (x \leq 0.20)$. A. MAURER AND G. COLLIN. Laboratoire de Chimie Minérale Structurale, Faculté des Sciences Pharmaceutiques et Biologiques de Paris V 4, avenue de l'Observatoire, 75270 Paris Cedex 06, France. The structural, electrical, and magnetic properties of $Cr_{3\pm x}Se_4$ ($x \leq 0.20$) compounds are examined. The crystal structure of $Cr_{2.80}Se_4$, monoclinic distorted NiAs type, is determined on a single crystal ($R = 2.9\%$). Physical properties are influenced by the effects of nonstoichiometry; it leads to a separate discussion for compounds $Cr_{3+x}Se_4$ ($0 \leq x \leq 0.20$), metallic, antiferromagnetic, with a high g factor value on the Cr^{2+} site, and $Cr_{3-x}Se_4$ ($0 \leq x \leq 0.20$), poorly metallic, and metamagnetic. The results are interpreted on the basis of structural considerations.

Structural Correspondences and Mechanisms for the Polymorphic Transformations $NaCl \rightleftarrows CsCl$ type and $NaCl \rightleftarrows$ Rhombohedral. S. W. KENNEDY. Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, 5001 Australia. Experimental evidence is presented for a martensitic mechanism of transformation $(NaCl) \Rightarrow (CsCl)$ type in supercooled NH_4Br crystals. Two published structural relationships are shown to be equivalent to the original Shoji–Buerger correspondence. The effect of conditions on mechanism is discussed. Interface immobilization in transformations is attributed to relaxation of the interface structure.

An Electron Microscopy Study of Crystallography and Phase Relationships in the Be_3N_2–$BeSiN_2$ System. T. M. SHAW AND G. THOMAS. Department of Materials Science and Mineral Engineering, University of California, Berkeley, California 94720. Transmission electron microscopy and diffraction have been used to examine structural aspects of phases along the $BeSiN_2$–Be_3N_2 tie line of the Be–Si–O–N system. Electron diffraction experiments are found to substantiate previous X-ray evidence for the derived structures of $BeSiN_2$, β-Be_3N_2, and α-Be_3N_2 and the presence of a number of long-period superstructures at intermediate compositions. Real space observations using direct fringe and structure imaging techniques have been made and are in agreement with the 15R polytype structure derived from X-ray diffraction data. This structure is composed of coherent intergrowths of $BeSiN_2$ and β-Be_3N_2. Further observations made on a nonstoichiometric $BeSiN_2$ sample suggest that the polytypes may be described in terms of a regularly faulted $BeSiN_2$ structure. Each fault changes the coordination of tetrahedral sites from base sharing to edge sharing in the fault, allowing excess beryllium atoms to be accommodated in the close-packed nitrogen lattice. For larger deviations from the $BeSiN_2$ stoichiometric composition, a higher density of faults occur which interact to form ordered arrangements and the observed polytype structures. The present observations establish that polytypism in the Be–Si–N system is related to the general phenomenon of crystallographic shear as observed in other complex oxide and ceramic systems. It is suggested that similar faulting may account for the polytype structures in other sialon systems.

Un Niobate de Rubidium d'un Type Structural Nouveau: $Rb_4Nb_6O_{17} \cdot 3H_2O$. MADELEINE GASPERIN AND MARIE-THERESE LE BIHAN. Laboratoire de Minéralogie-Cristallographie, Université P. et M. Curie, 4 Place Jussieu, 75230 Paris Cedex 05, France. A new double oxide, $Rb_4Nb_6O_{17} . 3H_2O$, has been synthesized as single crystals. It crystallizes in the orthorhombic system, space group *Pmnb*, with unit cell dimensions $a = 7.83(1)$, $b = 39.06(5)$, $c = 6.57(1)$ Å. $Z = 4$. The structure was solved by X-ray diffraction using three-dimensional Patterson and Fourier techniques with 811 reflections collected on films. The least-squares refinement gives $R = 0.124$ for the 581 reflections with $F > \max/20$. The structure consists of sheets made of two planes of NbO_6 octahedra linked with one-half of the Rb atoms. The two other Rb atoms, placed on the surface and between the sheets, are surrounded with water molecules which, alone, provide the cohesion of the whole structure by Rb–H_2O–Rb bonds and by two H bonds with the oxygen atoms of the sheets. This disposition explains the cleavage and the mica-like appearance of the crystals.

Transitions de la Forme de Haute Temperature α de In_2Se_3, de Part et d'autre de la Temperature Ambiante. ANNA LIKFORMAN, PAUL HENRY FOURCROY, MICHELINE GUITTARD, JEAN FLAHAUT, RAYMOND POIRIER, and NICOLAS SZYDLO. Laboratoire de Physique et Laboratoire de Chimie Minérale Structurale, Faculté des Sciences Pharmaceutiques et Biologiques de l'Université René Descartes, 4 avenue de l'Observatoire, 75270 Paris Cedex 06, France. The high-temperature form of In_2Se_3, α, encompasses several hexagonal or rhombohedral polytypes, having the same fundamental basis, hexagonal $a_1 = 4.02$ Å and $c_1 = 9.56$ Å, and having c parameters which are integral multiples of c_1. The α form is stable above 550°C. Its transformation into γ-In_2Se_3 is relatively slow, and only possible just below the transition temperature—between about 400 and 550°C. At ordinary temperature, it exists in a metastable state, but on heating a transformation occurs at 200°C involving the formation of a new form, β-In_2Se_3, which seems also to be metastable. This again exists in several polytypic forms depending on the type of parent α form. The $\alpha(2)$ polytype has a metal/nonmetal transition at 200°K.

A Contribution to the Structural Chemistry of A-Type Rare Earth Sesquioxides. O. GREIS. Texas A & M University, College Station, Texas 77843. La_2O_3 and Nd_2O_3 have been annealed at temperatures between 1000 and 1600°C for decontamination. Only products annealed at least at these temperatures appeared to be monophasic. Both X-ray powder and electron single-crystal diffraction revealed the A-type sesquioxide structure. No difference could be found in samples either quenched or slowly cooled to room temperature. Two space groups, $P\bar{3}m1$ and $P6_3/mmc$, are reported for the *A*-type structure. X-Ray powder studies seemed to support the latter on the evidence of extinctions. Electron diffraction from single crystals, however, indicated the space group $P\bar{3}m1$ confirming the so-called Pauling structure, while $P6_3/mmc$ can be excluded now unequivocally.