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# Abstracts of Forthcoming Articles

*Etude Structurale et Magnetique des Oxydes Perovskites $Ba_2NbVO_6$ et $Sr_2TaVO_6$.* JEAN-CLAUDE BERNIER, CHRISTIAN CHAUVEL ET OLIVIER KAHN. Universite Louis Pasteur, Ecole Nationale Superieur de Chimie de Strasbourg, Département Science des Matériaux, B.P. 296/R8, 67 Strasbourg, France. Two new perovskites $Ba_2NbVO_6$ and $Sr_2TaVO_6$ are investigated. These compounds are prepared by solid state reaction between 1100°C and 1200°C in a special high temperature furnace. The crystallographic study on polycristalline powder samples gives the spatial group *Pm*3*m* for the 2 perovskites. Magnetic susceptibilities were determined in the temperature range 4.2–1200°K. Above 400°K a theoretical interpretation is proposed by magnetic exchange interaction between pairs of Vanadium. The parameters corresponding to this interpretation are calculated.

*Phases Multiples dans les Systèmes $Ca_2Nb_2O_7$–$NaNbO_3$ et $La_2Ti_2O_7$–$CaTiO_3$: les series homologues de formule $A_nB_nO_{3n+2}$.* MONIQUE NANOT, FRANCINE QUEYROUX, JEAN-CLAUDE GILLES, ALAIN CARPY, ET JEAN GALY. Université de Bordeaux, 351 cours de la Libération, 33405 Talence, France. Deux familles structurales $A_nB_nO_{3n+2}$ (A = Ca, Ca et Na ou La et Ca; B = Nb ou Ti) ($n = 4$, 5; 5; 6 et 7), dérivées de la pérovskite, ont été mises en évidence dans les systèmes $Ca_2Nb_2O_7$–$NaNbO_3$ et $La_2Ti_2O_7$–$CaTiO_3$. Les mailles cristallines se déduisent de la maille pérovskite ($a_0$) à l'aide des relations: $a_n = a_0$, $b_n = na_0\sqrt{2} + 2K$ et $c_n = a_0\sqrt{2}$ ($K \cong 2.25$ Å).

*Stability of the Tetrahedral Phase in Cu–Ge–Se System.* B. B. SHARMA AND HARI SINGH. Solid State Physics Laboratory, Delhi-110007, India. Cu–Ge–Se system has been investigated in the vicinity of the compound $Cu_2GeSe_3$ which is known to have a disordered tetragonal unit cell with $a = 5.591$ Å and $c = 5.485$ Å. The unit cell symmetry has been found to be very sensitive to Ge concentration, slight deficiency of "Ge" lowers the cell symmetry to monoclinic while excess of "Ge" raises it to cubic. The composition $Cu_2Ge_{0.85}Se_3$ has a monoclinic unit cell with $a = 5.512$ Å, $b = 5.598$ Å, $c = 5.486$ Å, and $\beta = 89.7°$, while the composition $Cu_2Ge_{1.55}Se_3$ is cubic with $a = 5.569$ Å.

The results of this investigation indicate that the structure and stability of the $A_2^IB^{IV}C_3^{VI}$ group of compounds (subscripts denote number of atoms while superscripts denote the group in the periodic table) depend on the valence state of the participating IV group elements which is known to exhibit variable valency (tetravalency and divalency). The tetravalent state favours more distorted but more stable phase while divalent state favours less distorted and less stable phases.

*Etude à Haute Temperature du Diagramme d'Equilibre du Système Forme par le Sesquioxyde de Lanthane avec le Sesquioxyde d'Yttrium.* JULIETTE COUTURES ET MARC FOEX. Laboratoire des Ultra-Refractaires, C.N.R.S., B.P.5, 66120 Odeillo, France. The study at high temperature up to the melting point of the system formed by lanthanum sesquioxide with yttrium sesquioxide shows the formation of several very extended solid solutions, each one corresponding to a form given in these conditions by rare earth sesquioxides.

The phases determined "in situ" at the high temperature are very different from those observed when the products are cooled down to room temperature. The influence of quenching and annealing is demonstrated, particularly with $LaYO_3$.

*Structural Aspects of the Metal-Insulator Transition in $V_5O_9$.* M. MAREZIO, P. D. DERNIER, D. B. MCWHAN, AND S. KACHI. Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974. $V_5O_9$, a member of the homologous series $V_nO_{2n-1}$, undergoes a metal-insulator transition with decreasing temperature at ~135°K. The structures of both phases have been refined at 298°K and 110°K from single crystal data. The triclinic structures ($P\bar{1}$) consist of layers of $VO_6$ octahedra extending indefinitely in the *a–b* plane and truncated by a shear plane after every 5 octahedra along the *c*-axis. The average V–O distances for the V atoms at 298°K are for independent atoms 1 through 6. 1.949, 1.959, 1.965, 1.973, 1.967, and 1.971 Å, respectively. At 110°K the distances are 1.929, 1.975, 1.954, 1.994,

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1.954, and 1.986 Å. These values are interpreted as evidence for charge localization in the insulating phase with alternate strings of $V^{4+}$ ions and predominantly $V^{3+}$ ions running along the pseudorutile $c$-axis ($3^+$-chain is atoms 6-4-2-4-6 and $4^+$-chain is 5-3-1-3-5). The oxygen atoms in the insulating phase relax toward $V^{4+}$ string in the $a_R$ and $b_R$ directions and away from the $V^{3+}$ string. The shear planes allow the vanadium atoms to move along the $c_R$ axis so as to compensate for the change in length of alternate chains. Short V–V distances comparable to those in $VO_2$ are not observed; however, the structure has multiple possible patterns of metal–metal-bonds due to edge sharing of octahedra both along the pseudorutile $c$ axis and between adjacent chains at the shear planes.

*Transition Metal Iodates–V: Preparation and Characterization of the Smaller Lanthanide Iodates.* K. NASSAU, J. W. SHIEVER, B. E. PRESCOTT, AND A. S. COOPER. Bell Laboratories, Murray Hill, New Jersey 07974. The $Ln(IO)_3 \cdot xH_2O$ compounds of Eu through Lu, including Y, were prepared by precipitation; thermal decomposition; and by crystallization from the gel, from ambient and boiling water, and from boiling $HNO_3$. Six groups of compounds were obtained and characterized by powder X-ray diffraction, DTA, TGA, and infrared spectroscopy.
Two distinct structures with $x = 0$ occur for the iodates; one occurs for Eu to Lu plus Y, and the other for Yb and Lu. Two distinct structures occur for $x = 2$; one occurs for Eu–Er plus Y, and the other for Tm–Lu. One structure with $x = 4$ occurs for Gd to Lu plus Y. An amorphous phase appears as an intermediate stage during the decomposition of the tetrahydrates. All of these phases (except the amorphous one) were prepared in single crystal form and structural data will be reported elsewhere. Only the tetrahydrates have been previously reported; other compounds previously reported appear to have been mixtures.

*Fluorine–Chlorine Interaction in Fluor-Chlorapatite.* P. E. MACKIE AND R. A. YOUNG. Georgia Institute of Technology, Atlanta, Georgia 30332. When fluorine is partially substituted for chlorine in chlorapatite, steric interactions between the F and Cl ions produce effects not directly predictable from the properties of the end members, fluorapatite and chlorapatite, alone. The proximity of the remaining chlorine ions causes some of the substituting fluorine ions to be located ~0.6 Å from their normal sites ($0, 0, \frac{1}{4}$ and $0, 0, \frac{3}{4}$) on the halogen ion column. Some of the chlorine ions are similarly shifted >0.2 Å farther away from $0, 0, \frac{1}{2}$. The details of the displacements have been determined from least-squares analyses of X-ray data from synthetic single-crystals. Two fluor-chlorapatite compositions were used, ~14% and ~34% substitution of $F^-$ and $Cl^-$ with excess halogen becoming incorporated to raise the $F/(F + Cl)$ ratios to 0.17 and 0.41, respectively. The substitution models developed are capable of explaining (i) the nonlinear effects of the fluorine–chlorine substitution and (ii) the initial stabilization and later inhibition of the monoclinic phase, with respect to the hexagonal phase, with increasing substitution of fluorine into the chlorapatite structure, and (iii) in part, the occurrence of halogens in excess of the stoichiometric two per unit cell.

*Etude Structurale de Quatre Nouvelles Perovskites au Cobalt.* D. HARARI, P. POIX, ET J. C. BERNIER. Laboratoire de Chimie minérale, Batiment 420, Faculté des Sciences, 91405 Orsay, France. Four new perovskite-type compounds have been prepared: $Sr_3Co_2TeO_9$, $Sr_3Co_2WO_9$, $Ba_3Co_2TeO_9$, are cubic with unit cell parameters: $a = 4.930$ Å, $a = 7.910$ Å, and $a = 8.181$ Å. $Ba_3Co_2WO_9$ is hexagonal with unit cell parameters $a = 5.728$ Å and $c = 14.050$ Å. $Sr_3Co_2TeO_9$, $Sr_3Co_2WO_9$ and $Ba_3Co_2WO_9$ are ferrimagnetic at low temperatures. The values of the Curie constants show that the trivalent cobalt exists as the 2 electronic configurations $(t_{2g}^6)$ and $(t_{2g}^4\, e_g^2)$.

*Converning the Activation Energy of Solid State Reactions.* N. N. OLEYNIKOV, YU. D. TRETYAKOV, AND A. V. SHUMYANTZEV. Department of Chemistry, Moscow State University, Moscow 117234, U.S.S.R. Determination of the activation energy of solid state reactions without accounting for changes in reagent defects leads one to obtain values of the energy of activation and the preexponential factor that are devoid of real physical significance. The behaviour of reacting systems is investigated with the help of $\ln k = f(1/T)$ diagrams for various lattice defect concentrations. A formula is derived which allows one to determine the solid state reaction rate constant for reacting systems with a constant concentration of lattice imperfections. Application of the derived equation is illustrated for the reaction $MgO + Fe_2O_3$ with reagents of different thermal prehistory.