Cristallisation de $LiFe_5O_8$ dans un Verre 0,9 $Li_2B_2O_4$–0,1 $LiFe_5O_8$. C. CHAUMONT AND J. C. BERNIER,* Départment Science des Matériaux, Ecole Nationale Supérieure de Chimie de Strasbourg, 1, rue Blaise Pascal, B.P. 296/R8, 67008 Strasbourg Cédex, France. X-Ray diffraction, transmission electron microscopy, and magnetic measurements are used to study the crystallization of an amorphous compound: $Li_2B_2O_4$ 90–$LiFe_5O_8$ 10 (mole%). The crystalline phase which first appears in the amorphous matrix is $LiFe_5O_8$. The average particle size (50 to 300 Å) may be controlled by varying the temperature of annealing and/or the time of annealing. The crystallization kinetics are similar to those of metallic glasses. The fraction transformed, x, as a function of time, satisfies the Johnson–Mehl–Avrami equation with an exponent n of 0.75. The activation energy for the crystallization process is approximately 0.6 eV. Both these values characterize a primary crystallization.

Thermodynamics of Solid Solution Formation in NiO–MgO and NiO–ZnO. P. K. DAVIES AND A. NAVROTSKY,* Department of Chemistry, Arizona State University, Tempe, Arizona 85281. High-temperature calorimetric measurements on the enthalpies of solution in molten $2PbO \cdot B_2O_3$ of $(Ni_xMg_{1-x})O$ permit calculation of the enthalpy of the zincite to rock salt transformation in ZnO and the enthalpies of mixing, relative to rock salt standard states, in the two solid solution series. The enthalpy of the zincite to rock salt transformation is 24,488 ± 3592 J mole^{-1} with a corresponding positive entropy change of 0.48 ± 3.3 J K^{-1} mole^{-1}. The small positive entropy change for the transformation necessitates a very flat and perhaps negative dP/dT slope for the phase boundary. Both solid solutions, when referred to rock salt standard states, show negative enthalpies of mixing. For $(Ni_xMg_{1-x})O$ the negative enthalpies of mixing are fitted by a subregular model, where $\Delta H_{mix} = X_A X_B (BX_A + AX_B)$, with $A = -21,971 ± 4953$ J mole^{-1} and $B = -5103 ± 1151$ J mole^{-1}. The associated negative excess entropies of mixing, calculated from the heats of mixing and previously measured activity–composition relations, are similarly modeled with $A = -10.7$ J. K^{-1} mole^{-1} and $B = +1.1$ J K^{-1} mole^{-1}. Negative enthalpies of mixing in $(Ni_xZn_{1-x})O$ conform to a regular solution model with $W = -13,520 ± 5581$ J mole^{-1}. The negative enthalpies of mixing are interpreted in terms of a tendency toward ordering in the solid solutions, the proposed ordering scheme finding support in spectroscopic, structural, and magnetic data. These tendencies toward order are used to explain observed phase relations and thermodynamic properties in some other systems, containing a transition metal cation and another ion of similar size, namely, carbonates, hydrated sulfates, and the systems CuO–MO (M = Mg, Co, Ni).

Crystal Structure of $K_3PCr_4O_{16}$: A Second Example of a Quaternary Phosphorus. M. T. AVERBUCH-POUCHOT, A. DURIF,* AND J. C. GUITEL, Laboratoire de Cristallographie, B.P. 166 X, 38042 Grenoble Cédox, France. $K_3PCr_4O_{16}$ in monoclinic (Cc) with the unit-cell dimensions $a = 9.512(6)$ Å, $b = 11.74(2)$ Å, $c = 14.74(2)$ Å, $\beta = 106.13(5)°$, and $Z = 4$. Crystal structure has been solved with a final R value of 0.055. The main interest of this atomic arrangement is the geometrical configuration of the PCr_4O_{16} anion: a central PO_4 tetrahedron sharing its four corners with CrO_4 tetrahedra. This phosphochromic anion provides the second example of a quarternary in a finite anion.

Etude Radiocristallographique et Calorimetrique des Transitions de Phase de Ag_8GeTe_6. A. KATTY, O. GOROCHOV,* AND J. M. LETOFFE, Laboratoire de Physique des Solides, 1, Place A. Briand, 92190 Meudon Bellevue, France. Powder and single crystals of Ag_8GeTe_6 phase have been prepared by direct synthesis and chemical vapor transport reaction (iodine), respectively. The low-temperature phase of this material has been investigated by differential scanning calorimetry analysis and X-ray diffraction. The phase transitions are interpreted as a result of low-temperature ordering of the Ag$^+$ ions.

Raman Spectra of Lanthanide Sesquioxide Single Crystals: Correlation between A- and B-Type Structures. J. GOUTERON, D. MICHEL, A. M. LEJUS,* AND J. ZAREMBOWITCH, Laboratoire de Chimie Appliquée de L'Etat Solide, Ecole Nationale Superieure de Chimie de Paris, 11, rue P. et M. Curie, 75231 Paris Cédox 05, France. Structures and Raman spectra of lanthanide sesquioxide single crystals

with A-type trigonal structure (La_2O_3, Pr_2O_3, Nd_2O_3, Sm_2O_3) and B-type monoclinic structure (Sm_2O_3, Eu_2O_3, Gd_2O_3) are compared. The B form (C_{2h}^3 or $C2/m$, $Z = 6$) derives from the A form (D_{3d}^3 or $P\bar{3}ml$, $Z = 1$) by a slight lattice deformation, implying a splitting of D_{3d} and C_{3v} atomic positions into less symmetrical C_{2h} and C_s sites. This close structural relationship allows one to relate the Raman active modes of the B-type crystals to vibrations of the A-type crystals and to deduce an interpretation of the complex B-type spectra from those of the simpler A-type spectra. Furthermore, it is shown that the frequency of the modes which mainly involve metal–oxygen stretching motion increases with the lanthanide atomic number in the A and B series. This evolution is interpreted in terms of increasing the compactness of the structure.

The Crystal Structure of α-SrMnO$_3$. K. KURODA,* N. ISHIZAWA, N. MIZUTANI, AND M. KATO, The Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152, Japan. α-SrMnO$_3$ crystallizes in the hexagonal system with unit-cell dimensions $a = 5.454(1)$ Å, $c = 9.092(2)$ Å, space group $P6_3/mmc$, $Z = 4$. The structure was solved by the heavy atom method; of 404 unique reflections measured by the counter method, 203 that obeyed the condition $|F_0| \geq 3\sigma(|F_0|)$ were used in the refinement to a conventional R value of 0.043. The structure consists of four close-packed SrO$_3$ layers in an $ABAC$ stacking sequence along the hexagonal c axis. Oxygen octahedra containing Mn^{4+} are grouped into face-sharing pairs linked by corner sharing within the cubically stacked "A" layer.

A New Tungsten Trioxide Hydrate, WO$_3$ · $\frac{1}{3}$H$_2$O: Preparation, Characterization, and Crystallographie Study. B. GERAND, G. NOWOGROCKI, AND M. FIGLARZ,* Université de Picardie, Départment de Chimie, 33, rue Saint Leu, 80039 Amiens, France. A new hydrate of tungsten trioxide, WO$_3$ · $\frac{1}{3}$H$_2$O has been obtained by hydrothermal treatment at 120°C of an aqueous suspension of either tungstic acid gel or crystallized dihydrate. This hydrate has been characterized by different methods. Crystallographic study was carried out from X-ray powder diffraction. The hydrate crystallizes in the orthorhombic system: $a = 7.359(3)$ Å, $b = 12.513(6)$ Å, $c = 7.704(5)$ Å, $Z = 12$. The existence of structural relationships between the hydrate, WO$_3$ · $\frac{1}{3}$H$_2$O, and the product of dehydration, hexagonal WO$_3$, has permitted us to propose a structural model in agreement with the experimental data. WO$_3$ · $\frac{1}{3}$H$_2$O must be regarded as an interesting compound because its dehydration leads to a new anhydrous tungsten trioxide, hexagonal WO$_3$.

High-Pressure Phase Relations of CsD$_2$PO$_4$. A. I. KINGON, J. B. CLARK,* AND K. GESI, National Physical Research Laboratory, P.O. Box 395, Pretoria 0001, South Africa. The high-pressure phase diagram of CsD$_2$PO$_4$ to 4.5 GPa and temperatures between 0 and 470°C is reported. Comparisons are made with CsH$_2$PO$_4$ and correlated with the isotope effect on the high temperature, high-pressure phase relations of KH$_2$PO$_4$.

Structure and Phase Transitions of the Lanthanide Metals. R. H. LANGLEY, Department of Chemistry, University of Wisconsin, River Falls, Wisconsin 54022. The structures and phase transitions of the lanthanide metals can be related to f orbital contributions to the bonding. With increasing availability of the f orbitals the structure sequence hexagonal closest packed, double hexagonal closest packed, δ-samarium, cubic closest packed, and body-centered cubic is observed. Increases in temperature and/or pressure result in an increased availability of the f orbitals, resulting in predictable phase transitions.