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 $A = -21{,}971 \pm 4953$ J mole^{-1} and $B = -5103 \pm 1151$ 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 $W = -13{,}520 \pm 5581$ 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