JOURNAL OF SOLID STATE CHEMISTRY **39**, 135–136 (1981)

Abstracts of Forthcoming Articles

Crystalline Structure and OH Torsional Motion in Calcium–Strontium Arsenate Apatites. P. F. Gonzalez-Diaz* and P. G. Fernandez, Instituto de Optica "Daza de Valdes," CSIC, Serrano, 121, Madrid 6, Spain. The crystalline structure of $Ca_{10-x}Sr_x(AsO_4)_6(OH)_2$ has been studied, and the lattice parameters determined. It has been found that the unit cell expands with x. Geometric parameters of the unit cell, which are defined in relation to the hindered rotation of the OH group around the c axis, have also been obtained. From the ir data, the torsional potential function in first and second approximations has been calculated. A method for computing that function in any order approximation is given. A semiempirical curve is found, relating the stretching and torsional motions for both the OH and OD groups.

Defect Structures in the Brannerite-type Vanadates. IV. The Crystal Structure of $Mn_{1-x}\phi_xV_{2-2x}Mo_{2x}O_6$; $x = 0.53$. R. Kozlowski* and K. Stadnicka, Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland. The crystal structure of $Mn_{1-x}\phi_xV_{2-2x}Mo_{2x}O_6$; $x = 0.53$ of the brannerite type has been refined to $R = 0.029$. The space group is $C2$. The bond length bond strength calculations indicate a short-range ordering of Mo^{6+} and vacancies, resulting in the formation of Mo–O–ϕ–O–Mo clusters which are distributed at random in the host vanadate structure.

Origin of the Yellow Color of Complex Nickel Oxides. G. R. Rossman,* R. D. Shannon, and R. K. Waring. Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125. Single-crystal optical absorption spectra of NiO, $NiTiO_3$, $NiWO_4$, NiV_2O_6, $NiNb_2O_6$, Ni_2SiO_4, $Ni_3V_2O_8$, $LiNiPO_4$, $Li_2Ni_2Mo_3O_{12}$, $SrNiTeO_6$, $LiScSiO_4$: Ni, $MgSiO_3$: Ni, and $(Mg,Ni)_2SiO_4$ are presented for the purpose of comparing the spectra of yellow and green Ni^{2+} compounds. Powder spectra of $NiTiO_3$, $NiWO_4$, NiV_2O_6, $NiNb_2O_6$, and $Ni_3V_2O_8$ in the ultraviolet region help elucidate the more intense charge transfer bands. Bright yellow color results when Ni^{2+} is in a six-coordinated site significantly distorted from octahedral symmetry. Increased absorption intensity occurs when the metal ion d–d bands are in proximity to an ultraviolet charge transfer band.

The Crystal Chemistry of the New Rare-Earth Sodium Borates $Na_3Ln(BO_3)_2$ (Ln = La,Nd). J. Mascetti, M. Vlasse,* and C. Fouassier, Laboratoire de Chimie du Solide, Université de Bordeaux I, 351, cours de la Libération, 33405 Talence Cédex, France. The ternary borate systems Na_2O–Ln_2O_3–B_2O_3 (Ln = La, Nd) have been investigated in view of obtaining high-neodymium-concentration materials with weak concentration quenching. A ternary phase of composition $Na_3Ln(BO_3)_2$ (Ln = La, Nd) has been found. It crystallizes in the monoclinic space group $P2_1/c$. The structure has been determined for $Na_3Nd(BO_3)_2$. A full-matrix least-squares refinement led to $R = 0.040$. The structure is formed by isolated BO_3 triangles held together by the neodymium and sodium ions. The rare-earth atoms have a complex eightfold coordination in a covalent BO_3 matrix.

Preparation and Properties of the System $Fe_{1-x}V_xNbO_4$. B. Khazai, R. Kershaw, K. Dwight, and A. Wold,* Department of Chemistry, Brown University, Providence, Rhode Island 02912. Members of the system $Fe_{1-x}V_xNbO_4$ were prepared and their crystallographic, electrical, and magnetic properties were determined. The wolframite structure is formed for $x \leq 0.2$, but for $x \geq 0.4$, a phase transformation to the rutile structure takes place. Magnetic studies established the formal valencies of the elements for members crystallizing with the wolframite phase. However, similar analyses of compounds with the rutile structure did not provide a unique assignment of the formal valencies.

Mechanism of Ni–Zn Ferrites Formation. V. V. Pan'kov and L. A. Bashkirov,* Institute of Solid State Physics and Semiconductors, Byelorussian Academy of Sciences, Minsk, Podlesnaya 17, 220726, USSR. The regularities in the change of character of the ferrite formation process as a function of $Ni_{1-x}Zn_xFe_2O_4$ solid solution and of the degree of zinc oxide saturation of the $Ni_{1-x}Zn_xO$ solid

Note. Asterisks indicate author to be addressed.

0022-4596/81/100135-02$02.00/0

solution ($x = 0.14$; 0.29; 0.43) are established in the temperature range 1220–1305°C. It is shown that in the reaction zone of interacting NiO, (Ni, Zn)O, or ZnO with Fe_2O_3 the ferrite phase crystallizes only on iron oxide. The distribution of the Fe, Ni, and Zn concentrations over the reaction layer thickness using electron probe and X-ray spectrum analysis is obtained. The interdiffusion coefficients over the investigated temperature range calculated in the (Ni, Zn, Fe)O and ferrite phases change from $(0.8–7.0) \times 10^{-9}$ to $(1.0–12.0) \times 10^{-10}$ cm^2/sec, respectively. The interaction of (Ni, Zn)O with Fe_2O_3 takes place by the mechanism of interaction of interdiffusion of Fe^{3+}, Fe^{2+}, and Ni^{2+}, Zn^{2+} along with a current of Zn^{2+} ions and electrons or oxygen ions directed to the ferrite/Fe_2O_3 interface.

Phase Equilibrium Relations in the Binary systems $LiPO_3$–CeP_3O_9 and $NaPO_3$–CeP_3O_9. M. Rzaigui and N. Kbir Ariguib,* Laboratoire de Physico-Chimie Minérale, Ecole Normale Supérieure, 43, Rue de la Liberté, Le Bardo, Tunis. The $LiPO_3$–CeP_3O_9 and $NaPO_3$–CeP_3O_9 systems have been investigated for the first time by DTA, X-ray diffraction, and infrared spectroscopy. Each system forms a single 1:1 compound. $LiCe(PO_3)_4$ melts in a peritectic reaction at 980°C. $NaCe(PO_3)_4$ melts incongruently, too, at 865°C. These compounds have a monoclinic unit cell with the parameters: $a = 16.415(6)$, $b = 7.042(6)$, $c = 9.772(7)$ Å, $\beta = 126.03(5)°$, $Z = 4$, space group $C2/c$ for $LiCe(PO_3)_4$ and $a = 9.981(4)$, $b = 13.129(6)$, $c = 7.226(5)$ Å, $\beta = 89.93(4)°$, $Z = 4$, space group $P2_1/n$ for $NaCe(PO_3)_4$. It is established that both compounds are mixed polyphosphates with chain structure of the type $|M_I^I M_{II}^{III} (PO_3)_4|_\infty$ M_I^I: alkali metal, M_{II}^{III}: rare earth.

Phase Relations in the Ternary W–Mo-O System. T. Ekström, E. Salje, and R. J. D. Tilley,* School of Materials Science, University of Bradford, Bradford BD7 1DP, West Yorkshire, United Kingdom. The phases in the ternary W–Mo–O system have been determined using X-ray diffraction and electron microscopy. Series of mixed crystals occur for the fully oxidized compounds $W_xMo_{1-x}O_3$. Slightly reduced crystalline samples consist of *CS* phases containing {102} *CS* planes which are ordered when the Mo content is high. These latter have overall compositions $(W_xMo_{1-x})_n O_{3n-1}$, with n increasing with increasing W-content from 9 to 16. More substantially reduced crystals show less tendency to form mixed crystals. In samples of overall composition near to $M\ O_{2.90}$ phase separation occurs into {102}-containing *CS* phases which are molybdenum rich and {103} *CS* phases which are tungsten rich. The tungsten oxides $WO_{2.82}$ and $W_{18}O_{49}$ seem to contain little or no Mo. These results are summarized in a phase diagram.

The Structure of Cubic $YbZrF_7$. M. Poulain and B. C. Tofield,* Materials Development Division, AERE Harwell, Oxon, OXll ORA, United Kingdom. The structure of primitive-cubic $YbZrF_7$ has been determined using X-ray and neutron diffraction techniques. A unit cell ($a = 4.07$ Å, space group $Pm3m$) contains one formula unit of $Yb_{0.5}Zr_{0.5}F_{3.5}$, with no ordering of cations, in materials prepared by rapid quenching from 1000°C. Metal and fluorine displacements from ideal sites are in accord with results previously obtained on $Zr_{0.8}Yb_{0.2}\ F_{3.2}O_{0.3}$. The separation between F–F pairs bridging neighboring metal ions is similar to those observed in other complex zirconium fluorides. The metal displacements, metal–fluorine distances and fluorine–fluorine distances are discussed with respect to the formation and stability of disordered fluorine-excess ReO_3-type phases. These materials are intermediate in character between phases such as monoclinic $YbZrF_7$, with perfect order on both metal and nonmetal sublattices, and ZrF_4-based glasses, where there is disorder on the metal as well as on the fluorine sublattice. No ordering effects are observed on heating to near 200°C, but near 400°C there is a slow transformation to the monoclinic $YbZrF_7$ structure.