

followed by a sharp increase to about 85 kcal per mole of O_2 around $PrO_{1.78}$. No difference in partial molar enthalpy is observed between the oxidation and reduction paths within experimental error, even though different equilibrium pressures are observed depending on the path. The slight increase in the partial molar enthalpy in the "two-phase" region is attributed to the interaction term of the different domains using the same regular solution model as has been used to account for the hysteresis observed previously. The sharp change in $-\Delta\bar{H}_{O_2}$ around $PrO_{1.78}$ is believed associated with the phase change from the coherently intergrown ordered phases to the disordered alpha phase. The difference between the partial molar entropy on oxidation and reduction is explained by both the regular solution model and the usual thermodynamic treatment using the data of isothermal hysteresis.

Quasi-Chemical Treatment of Intermediate Phase Appearing in Nonstoichiometric Compounds.

JUN TATENO, Japan Atomic Energy Research Institute, Tokai-mur, Naka-gun, Ibaraki-ken, Japan. A quasi-chemical treatment of the superlattice formation model is applied to intermediate phases appearing in nonstoichiometric compounds. Two kinds of interaction energy are introduced and both intermediate phase and two-phase separation are described in a single formula. The order parameter and the free energy are obtained as a function of temperature and of composition. The boundaries of phases are determined by the common tangent method.

The System $BaO-SnO_2-Fe_2O_3$ with less than 50 mole% BaO at $1200^\circ C$ in Air, a Crystallographic Study. M. C. CADÉE* AND D. J. W. IDO, Section of Solid State Chemistry, Gorlaeus Laboratories, Leiden State University, P.O. Box 9502, 2300 RA Leiden, The Netherlands. The $BaO-SnO_2-Fe_2O_3$ system has been investigated after heating at $1200^\circ C$ in air. The mole percentage BaO was less than 50%. In the part of the system examined five quaternary compounds were determined: $BaSn_2Fe_4O_{11}$, $Ba_3SnFe_{10}O_{26}$, $Ba_{0.69}Sn_{2.62}Fe_{1.38}O_8$, $BaSn_{0.90}Fe_{3.47}O_{11}$, and a compound of still unknown composition; the best approximation is $BaSn_{1.70}Fe_{2.75}O_{8.32}$. The compounds were recognized by their X-ray diffraction patterns. All X-ray powder diffraction patterns could be indexed. No indication was found for reduction of Fe^{3+} to Fe^{2+} at $1200^\circ C$. A solid solution of perovskite compounds was found in the system $Ba_2Fe_2O_5-BaSnO_3$, caused by oxidation of Fe^{3+} to Fe^{4+} . This oxidation was observed also in the area $Ba_2Fe_2O_5-BaFe_2O_4-BaSnO_3$. The triangulation found in the $BaO-SnO_2-Fe_2O_3$ system is discussed and the system is compared with the $BaO-TiO_2-Al_2O_3$ system.

Crystal Structure and Pyroelectric Coefficient of $Co(IO_3)_2$ and Structural Relationships among the Anhydrous Noncentrosymmetric 3d-Transition Metal Iodates. C. SVENSSON, S. C. ABRAHAMS,* AND J. L. BERNSTEIN, Bell Laboratories, Murray Hill, New Jersey 07974. Cobalt iodate, $Co(IO_3)_2$ is pyroelectric at room temperature and crystallizes in the trigonal space group $P3$ with four formulas in the unit cell. The pyroelectric coefficient $p_3 = 5.1(5) \times 10^{-5} C m^{-2} K^{-1}$, and the lattice constants at $298 K$ are $a = 10.9597(1)$ and $c = 5.0774(1) \text{ \AA}$. The crystal structure was solved from the Patterson function and a consideration of the structural similarities among the anhydrous 3d-transition metal iodates. Refinement was by the method of least squares using 1825 observed reflections measured with a four-circle diffractometer. The final agreement factor $R = 0.050$. Two of the three independent octahedrally coordinated cobalt atoms are disordered. The absolute orientation of the polar axis was determined with respect to the crystal morphology. The iodine atoms in the trigonal pyramidal iodate ions point toward the morphologically undeveloped end of the crystals, as does the positive sense of the spontaneous polarization: It is this end that develops a positive polarization on heating. The spontaneous polarization is estimated at about $22 \times 10^{-2} C m^{-2}$. The iodate ion arrangement is very similar to that in $\alpha-LiIO_3$. The anhydrous noncentrosymmetric 3d-iodates may be classified into three isomorphous sets, with space group $P6_3$ and corresponding maximal subgroups $P3$ and $P2_1$. All three sets are isostructural with $\alpha-LiIO_3$ except for the cation distribution. The ability of the iodate ion framework to accept a range of cations of different valences is discussed in terms of the tricapped trigonal-prismatic environment about the iodine atoms.

Solid Solutions of $Pb_8M_2(XO_4)_8$ Lead Alkali Apatites. I. MAYER,* S. COHEN, AND J. R. MATALON, Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel. The $Pb_8Na_{2-x}K_x(PO_4)_8$, $Pb_8Na_{2-x}K_x(AsO_4)_8$, $Pb_8Na_{2-x}Rb_x(PO_4)_8$, and $Pb_8K_{2-x}Rb_x(PO_4)_8$ systems were studied. The compounds crystallize at all compositions in the $P6_3/m$ hexagonal apatite structure and

form true solid solutions. The change of the lattice parameters of the compositions and of the c/a values and their relation to the ionic radii of the alkali ions are discussed.

Free Energies of Formation of Metal-TCNQ Anion Radical Salts. S. ARONSON* AND J. S. MITTELMAN, Department of Chemistry, Brooklyn College, City University of New York, Brooklyn, New York 11210. Free energies of formation are determined for the TCNQ anion radical salts of Li, Na, K, Ba, Ag, Cu, Ni, and Pb. Aqueous electrochemical cell measurements at room temperature are used. The results are qualitatively similar to data on the corresponding metal iodides.

Phase Transitions and Surface Stability of the WO_3 - γ - Al_2O_3 System. P. TITTARELLI,* A. IANNIBELLO, AND P. L. VILLA, Stazione Sperimentale per i Combustibili, Viale De Gasperi 3, 20097-S. Donato Milanese, Milan, Italy. The solid-state transitions of the WO_3 - γ - Al_2O_3 system have been investigated in the temperature range 873–1323 K. The formation of α - Al_2O_3 and $Al_2(WO_4)_3$ phases and the thermal desorption of W(VI) attached to γ - Al_2O_3 have been studied as function of the treatment time. The inhibition of the phase transition to α - Al_2O_3 and therefore the stabilization of the surface has been observed at 1323 K for samples with 7% WO_3 content. This stabilization is critically affected by the tungsten content. An explanation for the stabilization of the alumina surface is proposed.

Hydroxyhydrogénosels: Le phosphate et l'arséniate non stoechiométriques de formule idéale $Na_3Al(OH)(HXO_4)(XO_4)(X = P \text{ ou } As)$. F. D'YVOIRE* AND M. PINTARD-SCRÉPEL, Laboratoire de Chimie Appliquée, Université Paris-Sud, 91405 Orsay, France. An aluminum-sodium phosphate and the corresponding isotopic arsenate have been synthesized. Chemical analysis, density measurements, thermogravimetry, X-ray powder diffraction, and ir spectroscopy lead to the conclusion that they are nonstoichiometric hydroxyhydrogen salts of ideal formula $Na_3Al(OH)(HXO_4)(XO_4)(X = P, As)$, the nonstoichiometry being a result of the presence of cation vacancies which are compensated by protons. The monoclinic unit-cell parameters have been determined. The space group is $C2/m$, $C2$, or $Cm.Z = 4$.

Electrical and Optical Behavior of One-Dimensional Organic Conductors at High Pressures. ICHIMIN SHIROTANI,* AKIFUMI ONODERA, AND HIROYUKI ANZAI, The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan. Electrical and optical behavior of 10 one-dimensional organic conductors has been studied at high pressures. The electrical resistivity of the organic conductors decreases with increasing pressure in the low-pressure region and reaches each resistivity minimum. The lowest resistivity of TTF-TCNQ and TTF derivative salts at high pressures is much lower than that of other salts. For conducting TCNQ salts, a pressure-induced absorption band has been observed around $20 \times 10^3 \text{ cm}^{-1}$; it may be assigned to the new charge transfer band between TCNQ. A pressure-induced band is not found in TTF-TCNQ, but the change of spectra with pressure is observed around $12 \times 10^3 \text{ cm}^{-1}$. Above certain pressures, the electrical resistivity of the organic conductors increases rapidly with increasing pressure and drifts upward with time. These phenomena arise from the solid-state reaction. The differences of the physicochemical properties of one-dimensional organic conductors will be discussed.

The Isostructural γ -Sulfur Phase of Selenium-Sulfur, Se_nS_{8-n} . ROBERT A. BOUDREAU AND HELMUT M. HAENDLER,* Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824. Two new selenium-sulfur species, $Se_{1.1}S_{6.9}$ (yellow) and $Se_{3.7}S_{4.3}$ (orange), have been isolated as single crystals, and the corresponding structures have been determined. The space group is $P2/c$, and the parameters are $a = 8.34 \text{ \AA}$, $b = 13.11 \text{ \AA}$, $c = 9.30 \text{ \AA}$, $\beta = 123.9^\circ$, and $a = 8.40 \text{ \AA}$, $b = 13.26 \text{ \AA}$, $c = 9.37 \text{ \AA}$, $\beta = 124.5^\circ$, respectively. They are isostructural with γ -sulfur, having two distinct pairs of eight-membered rings in the unit cell. The selenium and sulfur atoms appear scrambled throughout all atomic positions, but are not scrambled equally. When atomic site occupancy data are combined with other data from the literature, a wide compositional continuum of γ -sulfur isostructures is revealed that extends from γ -sulfur to SeS. It appears unlikely that selenium-sulfur crystals exist having the γ -sulfur structure with more than half the atoms as selenium.

Determination Precise de la Structure de la Chiolite $Na_3Al_3F_{14}$ et Etude par RPE de $Na_3Al_3F_{14}:Cr^{3+}$. C. JACOBONI, A. LEBLE, AND J. J. ROUSSEAU,* Laboratoire de Spectroscopie du Solide, Faculté