

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