N° 456 C.S.P. Universite Paris-Nord et Ecole Centrale des Arts et Manufactures, 92290 Chatenay-Malabry, France. The structure of Pb_3O_4 at 293°K has been refined to an R value of 0.06, using 29 neutron diffraction data obtained from a powdered sample. Oxygen atoms are displaced in the quadratic cell (space group $P4_2/mbc$; $a = 8.811$ Å and $c = 6.563$ Å) with respect to previous results obtained by several authors. The interatomic Pb^{IV}–O and Pb^{II}–O distances are compared with those found in other lead oxides. While the oxygen octahedra around Pb^{IV} atoms are characterized by bondings a little too long, the divalent lead coordination is characterized by bondings a little too short.

Optical and Electronic Properties of Some New Rare Earth-Doped Lead Sodium Apatites. L. H. Brixner and P. E. Bierstedt. Central Research Department, E. I. duPont de Nemours and Company, Wilmington, Delaware 19898. Single crystals of the anion-deficient apatite of formula $Pb_8Na_2(PO_4)_6\phi_2$ as well as rare earth-doped compositions of the type $Ln_xPb_{8-x}Na_2(PO_4)_6\phi_{2-x/2}O_{x/2}$ with Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er have been grown by the Czochralski technique. All crystallize in the $P6_3/m$ space group of apatite with c_h about 7.20 Å and a_h about 9.73 Å. Transmission, excitation, and fluorescence spectra were obtained on many single crystals and are discussed. Anomalous dielectric behavior indicating ionic conduction is also presented. It is further shown that the often quoted "lead orthophosphate of apatite structure, $Pb_3(PO_4)_2$" is actually not pure lead phosphate but rather a sodium stabilized apatite of the composition $Pb_{8+x}Na_{2-x}(PO_4)_6\phi_{2-x/2}O_{x/2}$.

The Oxidation State of Iron in some Ba–Fe–S Phases: A Mössbauer and Electrical Resistivity Investigation of Ba_2FeS_3, $Ba_7Fe_6S_{14}$, $Ba_6Fe_8S_{15}$, $BaFe_2S_3$, and $Ba_9Fe_{16}S_{32}$. W. M. Reiff, I. E. Grey, A. Fan, Z. Eliezer, and H. Steinfink. Materials Science Laboratory, Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712. Mössbauer spectroscopy, electrical resistivity, and magnetic susceptibility results are used in conjunction with crystal structure information to characterize the oxidation state of iron in 5 phases formed in the Ba–Fe–S system. The compounds have as a common feature FeS_4 tetrahedra which articulate by edge and corner sharing into infinite chains or columns. In Ba_2FeS_3 and $Ba_7Fe_6S_{14}$ iron is divalent in the first compound and in the latter the ratio of Fe(II)/Fe(III) is 2:1 as expected by stoichiometry. The electrons are localized and Fe(II) and Fe(III) are in definite locations in the trinuclear $[Fe_3S_6S_{2/2}]$ unit. Delocalization of electrons occurs in $Ba_6Fe_8S_{15}$, $BaFe_2S_3$, and $Ba_9Fe_{16}S_{32}$ and these compounds have low electrical resistivities and display only one quadrupole doublet in the room temperature Mössbauer spectrum. The isomer shift values of 0.2 mm/sec and 0.6 mm/sec are diagnostic of high spin Fe(III) and Fe(II), respectively, when they are in tetrahedral coordination with sulfur; intermediate values are found when electron delocalization occurs.

Etude par Effet Mössbauer de la Structure et des Propriétés de Diffusion de la Phase Antifluorine Non-stoechiometrique: Li_8SnP_4. J. P. Motte and N. N. Greenwood. Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, England. The unit cell of $Li_{8+4x}Sn_{1-x}P_4$ ($-0.17 < x < +0.09$) results from an antifluorite superlattice with partial ordering of the tin atoms in space group $P\bar{4}3n$. Mössbauer spectroscopy, applied to 3 compositions ($x = -0.14$, 0, and 0.08), confirms the X-ray diffraction results with regard to tin distribution. Lithium atoms can be located on the different sites (tetrahedral and octahedral) from the fact that the isomer shift observed for the tin is a direct function of the occupation by lithium of the octahedral interstices. Mössbauer spectroscopy also establishes the characteristics of lithium diffusion in the lattice as a function of temperature and composition.

Some Thermodynamic Properties in Spinel Solid Solutions with the Fe_3O_4 Component. T. Katsura, M. Wakihara, S. Hara and T. Sugihara. Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan. Phase equilibria in $Fe–Fe_2O_3–Cr_2O_3$, $Fe–Fe_2O_3–V_2O_3$, $FeO–Fe_2MoO_4–Fe_3O_4$, and $FeO–Fe_2O_3–ZrO_2$ systems were precisely determined. On the basis of the present results, together with the $FeO–Fe_2O_3–TiO_2$ system studied by Taylor at 1300°C and by Webster and Bright at 1200°C, the following results were obtained (1) The solid solutions $Fe_2TiO_4–Fe_3O_4$, and $Fe_2MoO_4–Fe_3O_4$ are approximately ideal in respect to the activity–composition relation. (2) On the contrary, the solid solutions $FeCr_2O_4–Fe_3O_4$ and $FeV_2O_4–Fe_3O_4$ deviate significantly from Raoult's law, and these are of regular solution defined by Hildebrand.