

pound, and (b) the assumption of a fixed ratio of the two cationic species. It is shown that these two approaches are not equivalent, and that for the latter case, the activities of the binary constituents can vary widely with changes in the equilibrium nonmetal activity. For example, a ternary oxide with a fixed ratio of the two cationic components may be driven out of the single phase region by changes in ambient oxygen pressure, in effect transforming an initial case (b) to case (a), as defined above. BaTiO<sub>3</sub> is used as a specific example, and is discussed for the limiting case of negligible coulombic interaction between point defects.

*Study by Electron Microscopy and Electron Diffraction of Formation of Nickel Epitaxially Grown Catalysts.* G. DALMAI-IMELIK, C. LECLERCQ, AND A. MAUBERT-MUGUET. C. N. R. S., Institut de Recherches sur la Catalyse, 69626-Villeurbanne, France. In order to study the influence of the crystallographic arrangement at the surface of a metal supported catalyst on its catalytic properties, catalysts have been prepared with well-faceted nickel crystallites presenting particular faces at their surface. Catalysts were obtained by reduction by hydrogen of nickel antigorite evacuated at different temperatures. The morphology and structure of nickel antigorite, the parent of catalyst, has been determined by electron microscopy and electron diffraction at different temperatures. Rolled or flat sheets were observed. The texture of the catalysts obtained after reduction was determined. The crystallites of nickel are hexagonal platelets with either their [111] or their [110] plane parallel to the sheet support, depending on the conditions of preparation and reduction. Study of the orientations of [111] type or [110] type was done.

*Étude Structurale de Cs<sub>2</sub>SnF<sub>6</sub>.* J. DURAND, J. L. GALIGNE, AND A. LARI-LAVASSANI. Laboratoire de Chimie Minerale C and Laboratoire de Mineralogie et Cristallographie, Université des Sciences et Techniques du Languedoc, 34060 Montpellier, France. The Cs<sub>2</sub>SnF<sub>6</sub> structure is of the K<sub>2</sub>GeF<sub>6</sub> type (trigonal P $\bar{3}$ m1). The unit cell dimensions are  $a = 6.322(6)$  Å,  $c = 5.032(5)$  Å;  $Z = 1$ . Each tin atom is linked to six fluorine atoms at the corners of a nearly regular octahedron with Sn-F = 1.952(7) Å. The SnF<sub>6</sub><sup>2-</sup> anions are isolated. Each cesium atom is surrounded by 12 fluorine atoms. The final  $R$  index is  $R = 0.045$  from 453 X ray reflections.

*Magnetic Susceptibility of the One-Dimensional Conductor (H<sub>3</sub>O)<sub>1.6</sub>[Pt(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sub>n</sub>H<sub>2</sub>O.* D. HEITKAMP AND H. S. RADE. Institut für Chemie, Kernforschungsanlage Jülich. AND H. J. KELLER AND H. H. RUPP. Institut für Anorganische Chemie der Universität Heidelberg, Germany. The magnetic susceptibility of the dioxalatoplatinate acid (H<sub>3</sub>O)<sub>1.6</sub>[Pt(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sub>n</sub>H<sub>2</sub>O, a mixed valence planar (MVP) compound with columnar structure and one-dimensional metallic conduction properties, has been measured in the temperature range 1.5–300°K. The observed paramagnetism, like in other MVP-compounds, may be described by a linear 1/ $T$  dependence with a break in the slope at a characteristic temperature. The Curie constants as well as the point of discontinuity have been found to depend on the crystal water content. The results are discussed in terms of different theoretical concepts.

*Formation Energies of Schottky Defects in Alkaline Earth Oxides.* G. RAMANI AND K. J. RAO. Materials Science Division, National Aeronautical Laboratory, Bangalore-560017, India. Schottky defect formation energies of alkaline earth oxides have been calculated by the procedure of Mott and Littleton, employing two parameter repulsive potentials. It is found that the polarizability of oxygen ion must be substantially lower in the case of MgO to obtain meaningful defect formation energy. Use of both displacement and anion polarizabilities, obtained from respective dielectric data, for each oxide, yields defect formation energies that are in fair agreement with more recent experimental values, for all the alkaline earth oxides.

*The Electrical Conductivity of Ammonium Perchlorate Single Crystals.* A. G. KEENAN AND M. G. OHANIAN. Department of Chemistry, University of Miami, Coral Gables, Florida 33124. The electrical conductivity of single crystals of ammonium perchlorate has been studied from 25–180°C. Plots of log  $\sigma T$  versus 1/ $T$  show two linear regions, one from 25–100°C and another from 100–180°C. Activation energies for the conduction processes in the low and high temperature regions are 0.12 and 1.04 eV, respectively. The conduction is a bulk process and not a surface mechanism. Conduction in the low temperature region is predominantly due to the migration of protons and is sensitive to the concen-

tration of interstitial H<sub>2</sub>O molecules that act as proton donor and acceptor sites. In the high temperature region, conduction is due to migration of NH<sub>4</sub><sup>+</sup> through cation vacancies. Detailed mechanisms are postulated both for electrical conduction and for electrode reactions.

*Oxydes de Plomb. III. Étude par Diffraction des Rayons X sur Poudre Des Transitions Ferroelectrique et Ferroelastique de l'Oxyde Pb<sub>3</sub>O<sub>4</sub>.* P. GARNIER, G. CALVARIN AND D. WEIGEL. Laboratoire de Chimie/Physique du Solide, Université de Paris-Nord et Ecole Centrale des Arts et Manufactures, 92290 Chatenay-Malabry, France. About 20 X ray powder diagrams were recorded in the range 30–295°K, by means of a prototype diffractometer and a high-efficiency cryostat, so that a very precise study of the anisotropic structural evolution of lead oxide Pb<sub>3</sub>O<sub>4</sub> could be made. The cell parameters, the volume and the principal thermal expansion coefficients have been computed. On the thermal expansion curves, anomalies are observed at 225 and 170°K. Assumptions about the mechanism of the transitions are expressed.

*Influence de l'Insertion des Groupements Anioniques MO<sub>4</sub><sup>n-</sup> sur les Propriétés Cathodochromiques et Photochromiques des Sodalites.* A. LEVASSEUR, F. GUILLEN, C. FOUASSIER, AND P. HAGENMULLER. Laboratoire de Chimie du Solide du C. N. R. S., Université de Bordeaux I, 351 cours de la Libération, 33405 Talence, France. AND J. M. GUTIERREZ AND J. P. GALVES. Groupement Tubes Electroniques, Thomson-C. S. F., 38120 Saint-Egreve, France. The influence of MO<sub>4</sub><sup>n-</sup> (where M = P, S, Cr, Mo, or W) upon the cathodochromic properties of sodalites Na<sub>4-x+ny</sub>(AlSiO<sub>4</sub>)<sub>3</sub>X<sub>1-x</sub>(MO<sub>4</sub>)<sub>y</sub> (X = Cl, Br, I) has been investigated. The coloration contrast is increased in presence of PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, and WO<sub>4</sub><sup>2-</sup> anions. The energy levels of the anionic groups have been obtained from the photochromic behavior and they vary inversely with their oxidation power. An improvement of the cathodochromic properties is observed only when they lie above the valence band.

*Influence of Charge-Compensating Ions on the Luminescence of Vanadium-Activated Sulfates.* G. BLASSE AND G. P. M. VAN DEN HEUVEL. Physical Laboratory, Sorbonnelaan 4, Utrecht, The Netherlands. Samples CaSO<sub>4</sub>-V<sup>5+</sup>, Me<sup>3+</sup> show mainly unassociated-vanadate emission if Me<sup>3+</sup> is smaller than the Ca<sup>2+</sup> ion and mainly associated-vanadate emission if Me<sup>3+</sup> is about as large as the Ca<sup>2+</sup> ion. Samples MgSO<sub>4</sub>-V<sup>5+</sup>, Me<sup>3+</sup> show efficient yellow emission at room temperature.

*The Structures of Fluorides. XIII. The Orthorhombic Form of Tungsten Hexafluoride at 193°K By Neutron Diffraction.* J. H. LEVY, J. C. TAYLOR, AND P. W. WILSON. Australian Atomic Energy Commission, Research Establishment, Sutherland, N. S. W., 2232, Australia. The positional parameters in the orthorhombic phase of solid tungsten hexafluoride WF<sub>6</sub> have been determined by total profile analysis of a neutron powder pattern taken at 193°K. WF<sub>6</sub> at 193°K is orthorhombic, with space group *Pnma* (*D*<sub>2h</sub><sup>16</sup>) and *a* = 9.603(3), *b* = 8.713(4), and *c* = 5.044(3) Å at 193°K. The full-matrix least-squares refinement converged at *R* = Σ(|y<sub>o</sub> - (1/c)y<sub>c</sub>|)Σy<sub>o</sub> = 0.075, where *c* is the scale factor and y<sub>o</sub> is one of the 306 background-corrected intensities in range of one or more Bragg reflections along the pattern. The refinement showed that at this temperature WF<sub>6</sub> has the orthorhombic UF<sub>6</sub> structure. The mean W-F distance is 1.81 Å, and the mean F-F separation between octahedra is 3.12 Å. The results are compared with previous neutron profile studies of the orthorhombic phases of UF<sub>6</sub> and MoF<sub>6</sub> at 193°K, and with a neutron profile Kubic Harmonic analysis of the cubic form of WF<sub>6</sub> at 266°K. On the basis of these structural studies in this series of hexafluorides, reasons are given why MoF<sub>6</sub> and WF<sub>6</sub> have a high-temperature cubic phase, but UF<sub>6</sub> does not. Deviations from idealised h.c.p. coordinates in the orthorhombic phases are in a direction such that the fluorine atoms become strongly bonded to the metal atoms to form a molecular, rather than an ionic, lattice.

*Preparation and Characterization of New Ternary Compounds in the System BaO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.* J. P. GUHA AND D. KOLAR. Institute Jožef Stefan, University of Ljubljana, Ljubljana. AND B. VOLAVŠEK. College of Chemistry, Maribor, Yugoslavia. Three new ternary compounds, BaTi<sub>3</sub>Al<sub>2</sub>O<sub>14</sub>, BaTiAl<sub>6</sub>O<sub>12</sub>, and Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub> have been identified in the system BaO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and were characterized by X ray powder diffraction. BaTi<sub>3</sub>Al<sub>2</sub>O<sub>14</sub> has a tetragonal unit-cell with *a* = 7.025 Å, *c* = 10.156 Å, and *Z* = 2. The compound melts incongruently at 1500°C. BaTiAl<sub>6</sub>O<sub>12</sub> has also a tetragonal unit-cell with *a* = 10.07 Å, *c* = 9.107 Å, and *Z* = 4. The compound melts incongruently at 1560°C. Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub> has an orthorhombic unit-cell with *a* = 14.854 Å, *b* = 11.356 Å, *c* = 4.986 Å, and *Z* = 2. The compound dissociates in the solid state at 1440°C to yield BaTiAl<sub>6</sub>O<sub>12</sub> and BaAl<sub>2</sub>O<sub>4</sub>.