

paramagnetic to 4.2°K. The evidence suggests that PrAl₂ and CaAl₂ are electronically similar with regard to band structure and both differ in band structure from that in GdAl₂.

Crystal Structure and Magnetic Properties of Ba₂Ni₃F₁₀. M. LEBLANC, G. FERREY, AND R. DE PAPE, Laboratoire des Fluorures et Oxyfluorures Ioniques, Route de Laval, 72017 Le Mans Cedex, France. Ba₂Ni₃F₁₀ is monoclinic (space group *c2/m*) $a = 18.542(7) \text{ \AA}$, $b = 5.958(2) \text{ \AA}$, $c = 7.821(3) \text{ \AA}$, $\beta = 111^\circ 92(10)$. Ba₂Co₃F₁₀ and Ba₂Zn₃F₁₀ are isostructural. The structure has been refined from 995 reflections by full-matrix least-squares refinement to a weighted *R* value of 0.048 (unweighted *R*: 0.047). The three-dimensional network can be described either by complex chains connected to each other by octahedra sharing corners or with a 18L dense packing sequence. The basic unit (Ni₃F₁₀)⁴⁻ is discussed and compared to a different one existing in Cs₄Mg₃F₁₀. Antiferromagnetic properties of Ba₂Ni₃F₁₀ ($T_N = 50 \text{ K}$) are described.

Infrared Spectrum of Several Double Oxides with Corundum Structure Resulting from the Transformation of Lacunar γ Phases with a Spinel Structure. B. GILLOT, F. BOUTON, F. CHASSAGNEUX, AND A. ROUSSET, Laboratoire de Recherches sur la Réactivité des Solides, BP 138, 21004 Dijon, Cedex, France. When aluminum or chromium is substituted by Fe³⁺ ions in α -Fe₂O₃, all the ir bands gradually shift toward high frequencies. Alternatively, for the α phases of type (Fe₂Cr_{4-y}Al_y)O₉ the transition occurs sharply for a composition *y* close to 2. For α phases substituted by (Fe_{6-y}Cr_y)O₉-type chromium a linear variation of frequency with chromium content is observed. From ir data it has been shown that, under given temperature and time conditions, an α phase less rich in chromium than the initial product could be obtained by oxidizing iron chromite. The ir spectrum of the oxidation of pure magnetites whose size is between 1400 and 15 000 Å evolves versus the latter to yield either the γ -Fe₂O₃ or the α -Fe₂O₃ phase which can be formed from γ -Fe₂O₃ or by direct oxidation of Fe₃O₄.

Preparation and Mössbauer Effect of Cr_{1-x}Fe_xOOH (0 ≤ x ≤ 1.0) with the InOOH-Type Structure. K. YABUTA, N. KINOMURA, M. SHIMADA, F. KANAMARU, AND M. KOIZUMI, The Institute of Scientific & Industrial Research, Osaka University, Osaka 565, Japan. The complete solid solutions of Cr_{1-x}Fe_xOOH with the InOOH-type structure were synthesized under high pressures. They were antiferromagnetic with Néel temperatures 570 K for FeOOH, 454 K for Cr_{0.2}Fe_{0.8}OOH, 332 K for Cr_{0.4}Fe_{0.6}OOH, and 160 K for Cr_{0.6}Fe_{0.4}OOH determined by the Mössbauer effect measurements.

Synthese et Caracterisation Cristallographique et Physique d'une Serie de Composes ACu₃Ru₄O₁₂ de Type Perovskite. M. LABEAU, B. BOCHU, J. C. JOUBERT, AND J. CHENAVAS, Laboratoire de Génie Physique, ENSIEG, BP 46, 38402, Saint-Martin-D'Herès, France. A series of ruthenates with the perovskite-like arrangement has been synthesized. The general formula is (ACu₃)(Ru₄)O₁₂ where (ACu₃) and (Ru₄) occupy the A and B sites of the ideal ABO₃ perovskite structure, respectively; A = Na⁺, Ca²⁺, Sr²⁺, Cd²⁺, La³⁺, Pr³⁺, and Nd³⁺. The change of the A site charge is balanced by a change of the ruthenium valence (+3, +4, or +5). The stability of the structure is strongly related to the relative size of the cations on the dodecahedral and octahedral sites. The magnetic susceptibility of the compounds with A = Na, Ca, and La is temperature independent above 70°K (for Ca), 120°K (for La) or 220°K (for Na) (Pauli paramagnetism). Resistivity measurements made on sintered samples between 77 and 300°K confirm the metallic nature of these compounds.

Crystal Structure of Na₃PCr₃O₁₃ · 3H₂O, A New Type of Chromophosphoric Anion. M. T. AVERBUCH-POUCHOT, A. DURIF, AND J. C. GUITEL, Laboratoire de Cristallographie, CNRS 166X, 38042 Grenoble Cedex, France. We describe chemical preparation and crystal structure of a new sodium phosphochromate: Na₃PCr₃O₁₃ · 3H₂O. This salt is orthorhombic with $a = 11.72(3)$, $b = 14.89(3)$, $c = 16.59(3) \text{ \AA}$, and $Z = 8$, Space group: *Pbc2₁*. The final *R* value is 0.063 for 2133 independent reflexions. The main feature of this atomic arrangement is the existence of a new type of chromophosphoric anion: PCr₃O₁₃. Infinite chains of NaO₆ run along the *a* direction. A survey of some phosphochromates previously described by the authors is given.

Semiconductivity, Optical Properties, and EPR Spectra of Phenothiazine Derivatives in the Solid State. A. ORTIZ, J. I. FERNÁNDEZ-ALONSO, A. PARDO, AND J. LLABRES, Departamento de Química-Física y Química Cuántica, Universidad Autónoma de Madrid, Cantoblanco, Madrid, 34, Spain. The optical, EPR, and electrical properties of phenothiazine derivatives have been investigated as a function of R₂ substituents. Diffuse reflectance spectra show a charge transfer complex transition between 600 and

1100 nm. The EPR spectra show the existence of the radical cation with an unpaired electron per molecule, also there can be seen a dependence of the bandwidth on the R_2 substituents. Measurements of electrical conductivity show a semiconductor behavior in the studied temperature range, the values show as well a dependence of conductivity on R_3 . The estimation of the drift mobility of charge carriers seems to indicate a hopping mechanism for the charge conduction.

Paramagnetic Defects in α - $W_xV_2O_5$. JACQUES LIVAGE, CHAKIB R'KHA, DOMINIQUE BALLUTAUD, AND JEAN-CLAUDE GRENET, Spectrochimie du Solide, Université Paris VI 4, place Jussieu, Paris 5e, France. Paramagnetic defects in α - $W_xV_2O_5$ have been studied by ESR. A model is proposed where the unpaired electron arising from a valence induction effect remains localized on a single vanadium ion near the W^{6+} along the b direction. Introducing W^{6+} leads to a lattice distortion which is more important than in the case of Mo^{6+} . A slight displacement of vanadium along the a direction is observed in the defect, V^{4+} showing a stronger tendency toward octahedral coordination than V^{5+} .

Investigation of the Surface Composition of NiO-MgO Solid Solutions by X-Ray Photoelectron Spectroscopy. A. CIMINO, B. A. DE ANGELIS, G. MINELLI, T. PERSINI, AND P. SCARPINO, Laboratori Ricerche di Base, Assoreni, 00015 Monterotondo, Roma, Italy. The surface composition of NiO-MgO solid solutions has been investigated by XPS. It has been found that no appreciable deviation from bulk composition is present, or, if present, it goes in the direction of a slight depletion in Ni^{2+} ions at the surface. The approximations involved and the problems encountered in the determination of the surface composition of air-exposed oxide samples are discussed.

The Structure of Orthorhombic $Na_2Ti_9O_{19}$, A Unit Cell Twinning of Monoclinic $Na_2Ti_9O_{19}$, Determined by 1-MV High-Resolution Electron Microscopy. YOSHIO BANDO, MAMORU WATANABE, AND YOSHIZO SEKIKAWA, National Institute for Researches in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki 300-31, Japan. The crystal structure of the orthorhombic disodium nonatitanate, $Na_2Ti_9O_{19}$, has been determined on the basis of 1-MV high-resolution structure images, in which each site of the titanium and sodium atoms is clearly resolved. The crystal has an orthorhombic symmetry with lattice parameters $a = 12.2$, $b = 3.78$, and $c = 30.1$ Å. The space group of the crystal is either $Ccmm$ or $Cc2m$. The crystal structure of the orthorhombic nonatitanate is closely related to that of the monoclinic nonatitanate reported previously in which the structure contains the sodium titanium dioxide bronze-type units connected by the bridging TiO_6 octahedra. The orthorhombic crystal can be described in terms of a unit cell twinning of the monoclinic crystal. It is shown that migrations of sodium ions occur by electron beam irradiation.

Metal Telluromolybdates of the Type $MTeMoO_6$. P. FORZATTI AND P. TITTARELLI, Stazione Sperimentale per i Combustibili, 20097 S. Donato Milanese (Milano), Italy. The solid-state reactions of $M\text{MoO}_4$ ($M = \text{Mg}^{2+}$, Fe^{2+} , and Ni^{2+}) and orthorhombic TeO_2 were investigated. A new metal telluromolybdate MgTeMoO_6 was obtained in the case of Mg; its structure belongs to the orthorhombic system with unit cell dimensions $a = 5.262$ Å, $b = 5.028$ Å, $c = 8.880$ Å. $\text{Fe}_2(\text{MoO}_4)_3$ and a new compound were formed in the case of Fe. The new compound is made up with Fe^{3+} ions and its chemical formula cannot be recognized as FeTeMoO_6 . In the case of Ni a complex reaction mixture is obtained. An explanation is given of the ability of M^{2+} ions to form the metal telluromolybdates. The catalytic properties of MgTeMoO_6 are discussed and compared to those of the other metal telluromolybdates.

$Ba_3WFe_2O_9$ ($P6_3/mmc$) and $Ba_3WFe_2O_{8.42(5)}$ ($Fm3m$): Comparative Study of the Crystallographic and Magnetic Properties. G. MATZEN AND P. POIX, Département Science des Matériaux, 1, rue Blaise Pascal, B.P. 296/R8, 67008 Strasbourg Cedex, France. $Ba_3WFe_2O_9$ has a hexagonal structure which belongs to space group $P6_3/mmc$. Heated at 1350°C under a stream of helium, this compound gives an oxygen-deficient phase whose structure is an ordered cubic one (space group $Fm3m$). This passage from a hexagonal structure to a cubic one is consistent with the decrease of the Goldschmidt tolerance factor resulting from the Fe^{3+} partial reduction. $Ba_3WFe_2O_{8.42(5)}$ (cubic) was compared with $Ba_3WFe_2O_9$ (hexagonal) and $\text{Sr}_3WFe_2O_{8.85(3)}$ (cubic) as to the crystallographical and magnetic properties. The study of the thermal stability in air for $Ba_3WFe_2O_{8.42(5)}$ revealed a reoxidation in several steps and the existence of a new cubic compound, stable in air over a broad range of temperature, and whose formula may be written $Ba_3WFe_2O_{8.71(5)}$.