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Abstracts of Forthcoming Articles

Influence of Gas Phase on the Polymorphic Transformations in $CoMoO_4$. J. HABER AND J. SLOCZYNSKI. Research Laboratories of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland. Polymorphic transformation b-$CoMoO_4 \rightarrow a$-$CoMoO_4$ at 400°C was studied in the high temperature X-ray camera in nitrogen, propylene, and hydrogen. It was found that the transformation is inhibited in the reducing atmosphere due to the interaction of the reducing agent from the gas phase with crystal nuclei of the new phase. Being very reactive, they are rapidly reduced, their elimination from the surface of crystallites inhibiting the transformation.

Phasengleichgewichte in Interlanthanidenoxid-Systemen. U. BERNDT, D. MAIER, AND C. KELLER. Institut fur Radiochemie, Kernforschungszentrum 75 Karlsruhe, Postfach 3640, Germany. Investigations in the quasibinary systems $LaO_{1.5}$–$REO_{1.5}$(Ce–Lu,Y) and $YO_{1.5}$–$REO_{1.5}$(La–Lu) at $1250°C \leqslant T \leqslant 1550°C$ have shown that besides a perovskite compound ABO_3 (for $A = La \rightarrow$, $B = Y$, Ho–Lu) mixed oxide phases with hexagonal (A-type), monoclinic (B-type), and cubic (C-type) structures of varying phase widths exist. All four phases are only existent in the $LaO_{1.5}$–$HoO_{1.5}$($YO_{1.5}$) and $PrO_{1.5}$–$LuO_{1.5}$ systems. The mutual solubility of the individual lanthanide oxides strongly depends on the difference of the ionic radii of the elements, in general increasing with decreasing difference. Maximum phase widths of B-type mixed oxides at 1550°C occur at $RE = Tb$ for the $LaO_{1.5}$–$REO_{1.5}$ systems and at $RE = Nd$ for the $YO_{1.5}$–$REO_{1.5}$ systems. At 1400°C up to 9 mole% $EuO_{1.5}$ may be incorporated in the perovskite compound. For the $LaYO_3$–$LaErO_3$ series, a maximum phase width with regard to the La:(Y + Er)-ratio is to be observed at the 1:1 composition.

Elaboration et Proprietes Magnetiques de Monocristaux D'oxyde de Praseodyme Pr_2O_3. A. M. LEJUS AND R. COLLONGUES. CECM, 15 rue G. Urbain, 94400 Vitry sur Seine. J. C. BERNIER. ENSCS, BP 296/R8, 67008 Strasbourg, France. Single crystals of praseodymium oxide with hexagonal A structure were prepared by the Verneuil process. Paramagnetic susceptibility measurements have been performed for various orientations of the crystal with respect to the magnetic field at constant temperatures (5, 77, 300°K) as well as at increasing temperatures (5–1000°K). They show an exceptional magnetic anisotropy ($\chi \perp / \chi \| \simeq 12$ at 5°K). An interpretation of this phenomenon is proposed.

Defect Structure of Zn-Doped ZnO. K. I. HAGEMARK. 3M Central Research Laboratories, St. Paul, Minnesota 55133. A defect structure model has been proposed for Zn-doped ZnO. Two donors, a native donor, Zn_i, and an unknown donor, D, and a native acceptor, V_{Zn}, have been suggested as the major defects. The model accounts for the experimentally determined relationship between the concentration of electrons and the partial pressure of Zn. The unknown donor could be frozen-in oxygen vacancy, V_O, which thermodynamically cannot be distinguished from a foreign donor.

Topotactic Oxidation of Valentinite, Sb_2O_3, to Cervantite, Sb_2O_4; Kinetics and Mechanism. P. S. GOPALAKRISHNAN AND H. MANOHAR Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India. It has been shown earlier by the authors that the oxidation of orthorhombic valentinite to orthorhombic cervantite as well as the reverse reduction is a topotactic reaction, where the structure of valentinite is completely preserved in cervantite. Kinetic studies of the oxidation now have been done in a polycrystalline sample as well as in single crystals. The latter studies using hot stage microscopy have enabled the rates of the reaction along different crystallographic directions to be determined. On the basis of the structural and kinetic studies, a mechanism for the diffusion of oxygen atoms that involves the making and breaking of bonds between (pentavalent) antimony and these oxygen atoms has been proposed. The results show that the oxidation of valentinite to cervantite is an interesting example of a solid state reaction where the diffusion process for the oxidation is governed by structural considerations.

Correlation between the Entropies of Fusion and of Allotropic Transitions of Metals. S.-A. CHO. Department of Metallurgy and Materials Science, Instituto Venezolano de Investigaciones Cientificas, Caracas, Venezuela. The relations between the heats of fusion A_2(bcc) → Liquid, A_1(fcc) → Liquid, and A_3 (hcp) → Liquid, and the fusion temperatures of allotropic metals were established.

$$\begin{aligned} &A_2 \rightarrow \mathrm{L}: \Delta H_{f_1} = 1.74 T_{f_1} \quad &&\text{and} \quad &&\Delta S_{f_1} = 1.74 \\ &A_1 \rightarrow \mathrm{L}: \Delta H_{f_2} = 2.25 T_{f_2} \quad &&\text{and} \quad &&\Delta S_{f_2} = 2.25 \\ &A_3 \rightarrow \mathrm{L}: \Delta H_{f_3} = 2.42 T_{f_3} \quad &&\text{and} \quad &&\Delta S_{f_3} = 2.42 \end{aligned}$$

The results reveal that enthalpies and entropies of fusion of these metals are merely dependent upon the ultimate structural type of the modification of the solid phase at the fusion temperature. The differences of energy and entropy between the solid and liquid states at the fusion point are termed "Structural Energy Change" and "Structural Entropy Change" of fusion.

Domaines D'existence et Proprietes Magnetiques des Germaniures Ternaires Monocliniques $Fe_{1-x}Co_xGe$ et $Fe_{1-x}Ni_xGe$. C. LE CAER, G. LE CAER, AND B. ROQUES. Lab de Chimie Solide, Universite de Nancy I, Case Officielle no. 140, 54037 Nancy, France. The substitution of chromium, manganese, cobalt, and nickel in the monoclinic form of iron monogermanide has been tried in order to define the magnetic properties of this compound. The cobalt and nickel alloys stabilize this form at low temperature and the Mossbauer effect shows that these metals substitute iron in an ordered manner, successively in 2(*c*), 2(*a*), and 4(*i*) sites. The magnetic interactions in FeGe are confirmed. The perturbation of some germanium atoms by cobalt and nickel would explain the magnetic properties of the alloys.

Oxygen Vacancies in $Nb_{22}O_{54-x}$, $Nb_{25}O_{62-x}$, and $Nb_{28}O_{70-x}$. T. KIKUCHI AND M. GOTO. National Institute for Researches in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki, 300-31, Japan. The isolated oxygen vacancies in $Nb_{22}O_{54-x}$, $Nb_{25}O_{62-x}$, and $Nb_{28}O_{70-x}$ at temperatures above 1300°C were examined thermodynamically using gravimetric data obtained previously by Kimura. The concentration of oxygen vacancies in $Nb_{22}O_{54-x}$ and $Nb_{25}O_{62-x}$ was estimated from isothermal changes in weight and found to be proportional to $Po_2^{-1/2}$. With $Nb_{28}O_{70-x}$, on the other hand, the concentration of oxygen vacancies was proportional to $Po_2^{-1/4}$. These results can be explained well on the assumption that the main defects, which all depend upon the partial pressure of oxygen in the surrounding atmosphere, are oxygen vacancies with one trapped electron, quasifree electrons, and tetravalent niobium atoms.

Electrical Properies of Undoped and Doped Potassium Tetrafluoaluminate: $KAlF_4$. J. SCHOONMAN AND R. A. HUGGINS. Center for Materials Research, Stanford University, Stanford, California. The electrical conductivity of nominally pure $KAlF_4$ crystals, and of nominally pure and doped polycrystalline $KAlF_4$ samples, has been studied. The electrical conductivity is highly anisotropic. Intrinsic defects are generated according to a Frenkel mechanism in the potassium ion sublattice. Although BaF_2 and ZrF_4 increase the conductivity due to an increase in potassium ion vacancy concentration, deviations from stoichiometry may lead to fluoride conduction in the extrinsic conductivity region.

Electrical Conduction in the Sintered Oxides of the System Bi_2O_3–BaO. T. TAKAHASHI, T. ESAKA, AND H. IWAHARA. Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Nagoya, Japan. The electrical conduction in various phases of the system Bi_2O_3–BaO was investigated by measurement of AC conductivity and EMF of oxygen gas concentration cell and observations of X-ray diffraction patterns. High oxide-ion conduction was observed in the rhombohedral phase present in 20 ~ 25 mole% BaO and hole conduction was observed in the perovskite type phase based on $2BaO \cdot Bi_2O_3$. The oxide-ion conductivity of the 20 mole% BaO specimen was 1.1×10^{-2} mho/cm at 500°C, and the contribution of electronic conductivity to total conductivity was negligibly small in air. In the remaining range of composition, where the monoclinic and rhombohedral mixed phase was found for less than 20 mole% BaO and the rhombohedral and perovskite type structure mixed phase was observed for more than 28 mole% BaO, the conduction was attributed to oxide ion and electron hole. High oxide-ion conduction in the rhombohedral phase was considered to be due to an appreciable amount of oxide-ion vacancies in this phase.

Le Systeme $Ba_{0.725}Sr_{1.775}Nb_{5-x}Ti_xO_{15-x}F_x$: Explication de L'accroissement de Permittivite des Ceramiques Oxygenees Ferroelectriques pour un Faible Taux de Substitution en Fluor. J. Ravez, M. Dabadie, R. von der Mühll, and P. Hagenmuller. Lab de Chimie du Solide, Universite de Bordeaux, 33405, Talence, France. The simultaneous substitution of niobium by titanium and oxygen by fluorine in $Ba_{0.725}Sr_{1.775}Nb_5O_{15}$ leads to a continuous solid solution and a "tetragonal tungsten bronze" structure. The various compounds show ferroelectric–paraelectric transitions. For single crystals the Curie temperature, the spontaneous polarization, and the permittivity decrease with increasing fluorine content. However, for ceramics the dielectric constant at the Curie point increases at small substitution rates. This result is consistent with the increase of the compacity.

Application du Trace des Diagrammes D'impedance Complexe a la Determination de la Conductivite Ionique des Solutions Solides $Ca_{1-x}Y_xF_{2+x}$: Correlations entre Proprietes Electriques et Structurales. J. M. Reau, C. Lucat, G. Campet, J. Portier, and A. Hammou. Lab de Chimie du Solide, Universite de Bordeaux I, cours de la Liberation, 33405 Talence, France. The grahical representation of the complex impedance of a solid electrolyte, measured with an AC technique, allows an accurate determination of the resistivity and the activation energy. This method is applied to a $Ca_{1-x}Y_xF_{2+x}$ solid solution ($0 \leqslant x \leqslant 0.38$). Electrical and structural data are correlated.

Elaboration et Etude Structurale des Antimoniates de Terres Rares $Ln_2Ln'SbO_7$(Ln, Ln' = Lu, Y, Gd, ou Ga) a L'aide de la Sonde Ponctuelle Eu^{3+}. J. P. Faurie, G. Boulon, and M. C. Delaigue. Lab de Chimie Minerale, Universite de Clermont-Ferrand, France. Rare-earth antimonates $Ln_2Ln'SbO_7$ (*Ln*, *Ln'* = Lu, Y, Gd, or Ga) have been prepared with pyrochlore structure. Excitation and emission spectra of these host lattices doped with Eu^{3+}, reveal two sites for Ln^{3+} and Ln'^{3+}. The symmetry of these sites is not D_{3d} as in the pyrochlore structure but could be C_{3v}.

Obtention, Caracterisation, et Principales Proprietes de L'hydroxymethylate de Nickel. S. LeBihan, J. Guenot, and M. Figlarz. Lab de Chimie des Solides de l'Universite Pierre et Marie Curie, 4. Place Jussieu, 75230 Paris 05, France. By the action of methanol in an autoclave at ca. 200°C on a turbostratic hydrated nickel hydroxide, a new compound, nickel hydroxymethylate $Ni[(OH)_{2/3}(OCH_3)_{1/3}]_2$, was obtained. This compound cannot be made with crystallized hydroxide $Ni(OH)_2$. It must be pointed out that the reaction was not actually effected unless the turbostratic hydroxide contained some mobile water molecules. X-ray study of the hydroxymethylate permitted a structural scheme of this compound to be tentatively advanced. The unit cell parameters are $a = 3.114 \pm 0.001$ Å and $c = 22.41 \pm 0.08$ Å (hexagonal system). The formation mechanism is discussed especially by taking electron microscopy as a basis. Thermal decomposition and hydrolysis of the hydroxymethylate were investigated as well.

Effect of Prior Mechanical and Thermal Treatment on the Thermal Decomposition of Orthorhombic Ammonium Perchlorate. V. R. Pai Verneker and K. Rajeshwar. Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India. The effect of prior mechanical and thermal treatment on the isothermal decomposition of ammonium perchlorate has been studied in the temperature range 215–235°C. Prior compression or heating of the material is seen to result in a lengthening of the induction period and a decrease in the decomposition rate. The final extent of the decomposition also decreases from the usual 30% to ~20% for the materials subjected to prior treatment. A significant correlation is observed between the effects of prior treatment on the thermal reactivity and the broadening observed in the X-ray diffraction patterns and the infrared spectra of the materials subjected to prior compression and heating.

Etude Structurale de Ca_2NH par Diffraction des Rayons X, Diffraction des Neutrons, et Resonance Magnetique Nucleaire du Proton dans le Solide. J.-F. Brice, J.-P. Motte, A. Courtois, J. Protas, and J. Aubry. Lab de Chimie Minerale A, Universite de Nancy I, 54037 Nancy, France. The hydridenitride Ca_2NH crystallizes with a superstructure of the NaCl type, space group $Fd3m$, with $a = 10.13$ Å. The structure is established by three complementary physical methods: X-ray diffraction, proton nuclear magnetic resonance, neutron diffraction. The first method establishes the arrangement of calcium and nitrogen in the cell. The two other methods fix the hydrogens. A quarter of them are statistically distributed on interstitial sites 96(*g*). The idealized model of Ca_2NH is compared with the well-known types of superstructure derived from NaCl.

Magnetic Susceptibiltiy and Nuclear Resonance Studies of $Tb_xY_{1-x}P$. R. K. QUINN AND H. T. WEAVER. Sandia Laboratories, Albuquerque, New Mexico 87115. Magnetic susceptibility and nuclear resonance of ^{31}P studies have been made for $Tb_xY_{1-x}P$ ($x = 0.005, 0.05, 0.10$, and 0.30) in the temperature range from 4–300°K. In this concentration range cooperative magnetic effects are small and the susceptibility is essentially determined by free Tb spins. However, the resonance lines are very broad and the uniform spin polarization model is found inapplicable.