

Abstracts of Forthcoming Articles

Crystal Growth and Electrical Conduction of PbMoO₄ and PbWO₄. W. VAN LOO. Solid State Chemistry Department, Physical Laboratory, State University, Utrecht, The Netherlands. The phenomenon of the colouration of Czochralski-grown single crystals of PbMoO₄ and PbWO₄ is discussed. This colouration is supposed to be related with an intrinsic point defect. We propose that during the crystal growth a loss of oxygen occurs and consequently, oxygen deficient crystals are produced. The existence of electronic charge carriers at high temperatures and ionic majority defects in the oxygen sublattice is confirmed by conductivity measurements. The colour center is supposed to be an oxygen vacancy which has trapped one or two electrons. On the basis of this simple model various aspects of the colouration can be understood.

The Crystal Structure of Cobalt Orthophosphate, Co₃(PO₄)₂. J. B. ANDERSON, E. KOSTINER, M. C. MILLER, AND J. R. REA. Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268. The crystal structure of cobalt orthophosphate has been refined by full-matrix least-squares procedures using automatic diffractometer data to a residual $R = 0.039$ ($R_w = 0.058$). The space group is $P2_1/c$, with $a = 5.064(3)$, $b = 8.365(4)$, $c = 8.794(4)$ Å and $\beta = 120.98(3)^\circ$. Co₃(PO₄)₂ is isotypic with the previously reported γ -Zn₃(PO₄)₂ and Mg₃(PO₄)₂. Cobalt ions occupy two distinct coordination polyhedra, one five- and one six-coordinated, in a ratio of two to one. The structure is described in detail.

Structural Studies of Some Body-Centered-Cubic Phases of Mixed Oxides Involving Bi₂O₃. The Structures of Bi₂₅FeO₄₀ and Bi₃₈ZnO₆₀. D. C. CRAIG AND N. C. STEPHENSON. School of Chemistry, University of New South Wales, Kensington, N.S.W., Australia. The structures of the compounds initially reported to be 7.Bi₂O₃·ZnO and 96.Bi₂O₃·4Fe₂O₃, have been determined by X-ray methods. Three-dimensional absorption corrected diffractometer data were used and atomic parameters were refined by least-squares procedures. The structures are isomorphous, cubic with $a = 10.194(3)$ and $10.179(3)$ Å, respectively, and space group $I23$. Each Bi³⁺ ion is surrounded by five oxygen atoms which form an incomplete octahedral arrangement with Bi–O distances ranging from 2.07 to 2.60 Å. The 6s² inert electron pair completes the octahedron. The Bi³⁺ ions are vibrating anisotropically. Tetrahedral sites in the structures contain 61 and 46 electrons, respectively. These values are consistent with a statistical distribution of Zn²⁺ and Bi⁵⁺ ions or Fe³⁺ and Bi⁵⁺ ions on these sites. Molar ratios are derived which agree with the observed distributions of electron density and also give rise to perfectly stoichiometric systems, devoid of cationic or anionic vacancies. The compositions studied correspond to Bi₂₄³⁺Bi⁵⁺Fe³⁺O₄₀ and Bi₃₆³⁺Bi⁵⁺ZnO₆₀ and they are optical enantiomorphs. It is proposed that a reduction in the percentage composition of Bi₂O₃ leads to metastable phases, in which all atomic positions remain fully occupied but some tetrahedral sites contain Bi³⁺ ions. The end product of the series is γ -Bi₂O₃ in which 50% of these sites contain Bi³⁺ and the remainder Bi⁵⁺ ions. We believe that γ -Bi₂O₃ is Bi₁₂³⁺Bi⁵⁺O₄₀.

Magnetic Property in the System BaCo_{1-x}Ni_xO₃ ($x = 0 \sim 1$). Y. TAKEDA. The Institute of Scientific and Industrial Research, Osaka University, Osaka 565, Japan. The system of BaCo_{1-x}Ni_xO₃ ($x = 0 \sim 1$) with a two-layer hexagonal perovskite-type structure are prepared at an oxygen pressure of 2000 bar. The change in unit cell parameters is not linear. Magnetic measurements indicate that BaCoO₃, BaCo_{0.9}Ni_{0.1}O₃, and BaCo_{0.8}Ni_{0.2}O₃ are antiferromagnetic with $T_N = 8, 10$, and 10 K respectively.

Interstitial Superstructures in the Ta–D System. H. ASANO, Y. ISHINO, R. YAMADA, AND M. HIRABAYASHI. The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan. Ordered deuterium arrangements and order–disorder transformations of the tantalum deuterides in the range TaD_{0.50}–TaD_{0.78} have been studied by neutron diffraction and calorimetry at temperatures between –170 and 120°C. In addition to the disordered phase (α), are clarified three ordered phases based on the superstructures Ta₂D_{1+x}(β_1), Ta₄D₃(γ) and TaD(δ). The

Ta₂D_{1+x} structure is a nonstoichiometric form of the Ta₂D superstructure over the range $x < 0.5$. The γ -phase is formed below -70°C near Ta₄D₃, and transforms into the β_1 - and δ -phases, respectively, in the hypo- and hyperstoichiometric compositions. The δ -phase which exists beyond TaD_{0.75} changes to the disordered α -phase around 100°C .

The Electrical Conductivity of Single Crystals of Ag₂HgI₄. K. W. BROWALL AND J. S. KASPER. General Electric Research and Development, Schenectady, New York. Electrical conductivity measurements are reported for single crystal samples of Ag₂HgI₄ in the temperature range between -17 and 72°C . The results are interpreted in terms of two distinct regions of linear log conductivity vs reciprocal temperature behavior for β -Ag₂HgI₄, a phase transition region, and an α -Ag₂HgI₄ region. The data reaffirm the anomalously high preexponential and activation energy terms in the conductivity equation for α -Ag₂HgI₄ as compared with other AgI-type conductors. Thermo-emf measurements on polycrystalline Ag₂HgI₄ samples are also reported.

The Effect of Crystal Size on Chemical Hysteresis in Praseodymium and Terbium Oxides. A. T. LOWE, K. H. LAU, AND L. EYRING. Department of Chemistry, Arizona State University, Tempe, Arizona 85281. The effect of the variation of crystal size on chemical hysteresis in phase reactions has been investigated by means of thermogravimetric analysis. Series of isobars were followed at several different pressures and crystal sizes for the PrO_x-O₂ and TbO_x-O₂ systems. At higher temperatures, the extent of hysteresis decreased with increase in crystal size for both oxides. It was found that equilibrium was not attained in reactions occurring at lower temperatures. These experiments are contrasted with previous investigations using powdered samples. Some plausible explanations for the trends observed are discussed.

Mischkristallbildung und Kationenordnung im System Bleihydroxylapatit-Calciumhydroxylapatit. G. ENGEL, F. KRIEG, AND G. REIF. Fachhochschule Aalen, Fachbereich Chemie, 7080 Aalen, Postfach 1728, Germany. In the system Pb₁₀(PO₄)₆(OH)₂-Ca₁₀(PO₄)₆(OH)₂ there exists a complete series of solid solutions. Outstanding deviation from Vegard's law and a break in the dependence of the c -constants are to be found at the composition Pb₆^{II}Ca₄(PO₄)₆(OH)₂. Together with calculations of X-ray intensities they reveal the indicated ordering of Pb on the M^{II}(=6h)- and of Ca on the M^I(=4f)-positions of the apatite structure. The above 6:4 compound constitutes an analogy to nasonite and ganomalite. These minerals have structures related to the apatite type. The reason for the Pb²⁺ ordering is its tendency to form bonds with partially covalent character. The same cation is observed in two other apatite solid solutions, (Pb, Ca₁₀)(PO₄)₄-(SiO₄)₂ and (Pb, Ca)₈Na₂(PO₄)₆, respectively. Starting from Ca₁₀(PO₄)₆(OH)₂ there is a drastic reduction of thermal stability with Pb substitution. It leads to a minimum which approximates to the composition Ca₈Pb₂(PO₄)₆(OH)₂. The reason is the strong increase in the degree of dehydration to oxyapatite, and the subsequent decay of the apatite structure. On precipitation (Pb, Ca)-hydroxy apatites from aqueous solutions there is a strong enrichment of Pb in the solid. Under the conditions mentioned in the text the initial enrichment of Pb is appreciably reduced in the course of several hours. The distribution coefficient for these conditions approximates to $D = 25$.

A Microdomain Description of Defective Fluorite-Type Phases Ca_xM_{1-x}O_{2-x} (M = Zr, Hf, x = 0.1-0.2). J. G. ALLPRESS AND H. J. ROSSELL. CSIRO Division of Tribophysics, University of Melbourne, Parkville, Victoria, 3052, Australia. Electron diffraction patterns from cubic solid solutions of lime in zirconia and hafnia contain weak diffuse features in addition to the strong reflexions expected from the fluorite structure type. A comparison of these features with those found in patterns from annealed specimens suggests that the solid solutions contain domains embedded coherently in a number of specific orientations within the cubic matrix. Each domain is about 30 Å in diameter, and its structure corresponds to that of CaHf₄O₉. Calculations based on this model agree with the observed diffraction data.

Growth and Optical Properties of TiGaSe₂ and β -TlInS₂. T. J. ISAACS AND J. D. FEICHTNER. Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235. TiGaSe₂ and β -TlInS₂ were studied for crystal growth and optical properties. Both materials have wide transparency regions, from 0.61 to 20 μm for the former and 0.5-12.5 μm for the latter. X-ray studies of single crystals show that these compounds are monoclinic, space group $P2_1/m$. Raman spectra are presented.