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Abstracts of Forthcoming Articles

The Phase Relationship among Compounds $Ba_{1+x}Fe_2S_4$. J. S. SWINNEA AND H. STEINFINK.* Materials Science and Engineering Laboratories, Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712. The dependence of composition of the phases $Ba_{1+x}Fe_2S_4$ on sulfur vapor pressure and starting composition was investigated at 650, 747, and 800°C. The infinitely adaptive series $Ba_{1+x}Fe_2S_4$ spans the compositions $0.072 \le x \le 0.142$. The value of x decreases as the sulfur vapor pressure increases at a given temperature. Varying the ratio of Ba/Fe in the starting mixture has no effect on the $Ba_{1+x}Fe_2S_4$–sulfur fugacity relationship. The phase $BaFe_2S_4$ is not part of the infinitely adaptive series.

Mössbauer Spectra, Magnetic and Electrical Behavior of $Ba_{1+x}Fe_2S_4$ Phases. J. S. SWINNEA AND H. STEINFINK.* The Mössbauer spectra, magnetic and electrical properties of $Ba_{1+x}Fe_2S_4$ infinitely adaptive phases with $0.074 \le x \le 0.142$ and of $BaFe_2S_4$ were studied. The properties are highly anisotropic because of the presence in the structure of one-dimensional infinite chains of edge sharing FeS_4 tetrahedra. $BaFe_2S_4$ is a semiconductor, $E_g = 0.66$ eV; magnetic susceptibility can be fit by a one-dimensional Heisenberg model with spin $\frac{5}{2}$ and $J/k = -30°$K. The $Ba_{1+x}Fe_2S_4$ phases have Curie–Weiss behavior with an effective moment of about 2 B.M. The moment increases with x. These phases are metallic. The Mössbauer isomer shift varies linearly with valence, increasing with increasing x. The single quadrupole split absorption line characteristic of these compounds disappears at about 270°K and a complex spectrum consisting of overlapping hyperfine patterns appears at lower temperatures. Magnetic short-range ordering is responsible for this behavior although the susceptibility in this temperature range does not reflect this effect.

High Temperature Structural Investigation of the Delafossite Type Compound $CuAlO_2$. T. ISHIGURO,* N. ISHIZAWA, N. MIZUTANI, AND M. KATO. Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan. Crystal structure parameters were determined for the delafossite type compound $CuAlO_2$ at 295, 450, 600, 750, 900 and 1200°K with single-crystal high-temperature X-ray diffraction technique. Anisotropic refinements result in conventional R values of 0.021, 0.027, 0.029, 0.030, 0.032 and 0.036 at respective temperatures. Crystals of $CuAlO_2$ have the rhombohedral space group $R\bar{3}m$ with $a = 2.8584(7)$, $c = 16.958(3)$ Å and $Z = 3$ at 295°K. The mean thermal expansion coefficient for the dimension a is 11.0×10^{-6} K^{-1} about three times larger than 4.1×10^{-6} K^{-1} for c. In the structure, the AlO_6 octahedra are linked by their O–O edges and form AlO_2 layers perpendicular to the c axis with the thickness corresponding to the height of an octahedron. With increasing temperature, the AlO_6 octahedra expand along the directions of the basal plane, while expansion scarcely occurs along the c axis. The Cu atom lying between the AlO_2 layers shows a large anisotropic behavior in the thermal vibration. The temperature factor for Cu atoms in the basal plane was approximately two times larger than that along the c axis at 295°K, and the ratio of the temperature factor perpendicular to c to that parallel to c becomes larger with increasing temperature.

An Outline of the Structure of New Layered Bismuth Lanthanum Tungstate, $Bi_{2-x}La_xWO_6$ ($x = 0.4$–1.1). A. WATANABE,* Y. SEKIKAWA, AND F. IZUMI. National Institute for Research in Inorganic Materials, 1-1 Namiki, Sakura-mura, Niihari-gun, Ibaraki 305, Japan. An outline of the structure of a continuous solid–solution series $Bi_{2-x}La_xWO_6$ with $x = 0.4$–1.1 (space group $P2/c$ and $Z = 8$) has been determined from a lattice imaging method of electron microscopy. A high-resolution lattice image of $Bi_{1.4}La_{0.6}WO_6$ selected as representative of the series showed that the structure consists of a regular stacking of $Bi_{1.4}La_{0.6}O_2$ layers interleaved with WO_4 layers. A structural model of $Bi_{2-x}La_xWO_6$ was proposed and atomic coordinates were estimated on the basis of the model. The structural relations between $Bi_{2-x}La_xWO_6$ and Bi_2WO_6 were discussed.

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Über den Mechanismus der Mechanochemischen Synthese Anorganischer Verbindungen. CHR. G. TSCHAKAROV,* G. G. GOSPODINOV, AND Z. BONTSCHEV. Lehrstuhl für Physik, Chemisch-Technologische Hochschule, BG-8010, Burgas, Bulgaria. In the present paper some data on phenomena observed during the mechanochemical synthesis of metal chalcogenides are given. The explosive-like character of the synthesis as a result of continual accumulation of energy in the crystal lattice of the substances submitted to mechanical dispersion is described for the first time. The influence of different factors on the time until explosion takes place is investigated.

Studies on the Effects of Doping Caesium Metal(III) Halides of the Type $Cs_3M_2^{III}X_9$ *(*M^{III} *= Sb or Bi,* X *= Cl or Br).* S. J. CLARK,* J. D. DONALDSON, AND D. R. LAUGHLIN. Department of Chemistry, The City University, Northampton Square, London ECl, England. A series of compounds, $Cs_3M_2^{III}X_9$ (M^{III} = Sb and Bi, X = Cl and Br) are doped with impurity ions (Ba^{2+}, Ca^{2+}, Sn^{2+}, Pb^{2+}, Mg^{2+}, Fe^{2+}, Tl^{3+}, In^{3+}, Se^{4+}). Lattices doped with Sn(II), Pb(II) and Se(IV) are colored. Sn-119*m* Mössbauer data are consistent with the donation of Sn-5*s* electron density from tin(II) to a conduction band to give a pseudo-tin(IV) electronic environment.

Experimental Study of Gases Occluded within Microscopic Cavities in Single Crystalline Nickel Oxide. R. FARHI,* G. PETOT-ERVAS, C. PETOT, G. DHALENNE, AND F. LE GUERN. Laboratoire des Propriétés Mécaniques et Thermodynamiques des Matériaux, Université Paris-Nord, 93430, Villetaneuse, France. The existence of microcavities (1–10 μm) in single crystalline nickel oxide was demonstrated by microscopic observations, and their effect on electrical conductivity described elsewhere. It was proposed that the anomalous conductivity values could be attributed to the presence, within the cavities, of oxygen gas under high pressure. In order to confirm this assumption, Raman microprobe and gas phase chromatography experiments have been performed on NiO single crystals. The results obtained concerning the gases detected (oxygen and nitrogen) are in qualitative and quantitative agreement with the microscopic observations and the electrical conductivity measurements.

$(NH_4)_4P_4O_{12} \cdot 2Te(OH)_6 \cdot 2H_2O$*, the First Example of a Tetrametaphosphate-tellurate.* A. DURIF,* M. T. AVERBUCH-POUCHOT, AND J. C. GUITEL. Laboratoire de Cristallographie, B.P. 166 X, 38042 Grenoble Cédex, France. Ammonium tetrametaphosphate-tellurate dihydrate: $(NH_4)_4P_4O_{12} \cdot 2Te(OH)_6 \cdot 2H_2O$ is triclinic with the following unit cell dimensions: a = 11.845(6), b = 8.554(5), c = 7.433(5) Å, α = 66.28(5), β = 95.91(5), γ = 76.00(5)°. Space group: $P\bar{1}$ and Z = 1. The crystal structure has been determined with a final R value 0.021. As in the already-described phosphate-tellurates: monophosphate-tellurates and trimetaphosphate-tellurates, the phosphoric anion (here the P_4O_{12} ring) is independent of the octahedral $Te(OH)_6$ group. A complete pattern of the hydrogen bonds is given.

Polymorphism in Bi_2WO_6*.* A. WATANABE. National Institute for Research in Inorganic Materials, 1-1 Namiki, Sakura-mura, Niihari-gun, Ibaraki 305, Japan. The polymorphism of Bi_2WO_6 has been studied using differential dilatometry and differential thermal analysis with polycrystalline specimens prepared by sintering the oxides Bi_2O_3 and WO_3. Two reversible polymorphic transitions were observed, one at 662°C and one at 962°C. The former transition showed a very small change of enthalpy and very little dimensional change, while the latter showed a large thermal hysteresis, had a large change of enthalpy and was accompanied by a sizable volume change. The high-temperature powder X-ray data indicated that the intermediate phase as well as the low-temperature form had orthorhombic symmetry and the high-temperature form had monoclinic symmetry. The 662°C transition is displacive and the 962°C transition reconstructive. The crystal structure of the high-temperature form was proposed and discussed in comparison with that of the low-temperature form.

$Ln(GaM^{2+})O_4$ *and* $Ln(AlMn^{2+})O_4$ *Compounds Having a Layer Structure [Ln: Lu, Yb, Tm, Er, Ho and Y, and M: Mg, Mn, Co, Cu and Zn].* N. KIMIZUKA* AND E. TAKAYAMA. National Institute for Research in Inorganic Materials, 1-1 Namiki, Sakuramura, Niiharigun, Ibaraki-ken, 305, Japan. A series of new compounds $Ln(GaM^{2+})O_4$ and $Ln(AlMn^{2+})O_4$ having a layer structure were successfully prepared [Ln: Lu, Yb, Tm, Er, Ho and Y, and M: Mg, Mn, Co, Cu and Zn]. The synthesis conditions and the unit cell parameters for 23 compounds have been determined. These compounds are isostructural with $YbFe_2O_4$ (S. G.: $R\bar{3}m$, a = 3.455(1) Å, and c = 25.109(2) Å).

Optical Transition Probabilities of Er^{3+} in Fluoride Glasses. R. REISFELD, G. KATZ, N. SPECTOR, C. K. JØRGENSEN,* C. JACOBONI, AND R. DE PAPE. Département de Chimie minérale, analytique et appliquée, University of Geneva, Switzerland. Lead-based fluoride glasses of the systems PbF_2–GaF_3–MF_2 (M = Zn or Mn) doped by trivalent erbium were prepared by melting and quenching of the appropriate fluorides under inert atmosphere. Optical spectra of the glasses with and without manganese reveal identical characteristics in the near-ir region of the spectrum. In the near-uv and visible part, the manganese-containing samples show higher oscillator strength, probably due to interaction between Mn^{2+} and Er^{3+}. Radiative and nonradiative characteristics of the glasses were computed, using the Judd–Ofelt method. Laser transitions of the glasses were predicted.

Über Ordnungs- Unordnungsphänomene bei Sauerstoffperowskiten vom Typ $A_3^{2+}B^{2+}M_2^{5+}O_9$. U. TREIBER AND S. KEMMLER-SACK.* Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, Germany. Perovskites of the type $A_3^{2+}B^{2+}M_2^{5+}O_9$, where A^{2+} = Ba, Sr; B^{2+} = Mn, Co, Ni, Zn; M^{5+} = Nb, Ta show order disorder phenomena. At lower temperatures a thermodynamically unstable disordered cubic perovskite is formed (⅓ formula unit—$AB_{1/3}M_{2/3}O_3$—in the cell), which transforms irreversibly into a 1 : 2 ordered high-temperature form with $3L$ structure (sequence $(c)_3$). For A^{2+} = Ba this lattice is hexagonal (space group $P\bar{3}m1$; one formula unit in the cell); with A^{2+} = Sr a triclinic distortion is observed. For $Ba_3CoNb_2O_9$ a second transformation into a cubic disordered perovskite takes place at 1500°C. This transition is reversible and of the order disorder type. The vibrational and diffuse reflectance spectra are discussed.

Electrical Conductivity in Calcium Titanate. U. BALACHANDRAN,* B. ODEKIRK, AND N. G. EROR. Oregon Graduate Center, 19600 N.W. Walker Road, Beaverton, Oregon 97006. The electrical conductivity of polycrystalline $CaTiO_3$ was measured over the temperature range 800–1100°C while in thermodynamic equilibrium with oxygen partial pressures from 10^{-22} to 10^{0} atm. The data were found to be proportional to the $-\frac{1}{6}$th power of the oxygen partial pressure for the oxygen pressure range 10^{-16}–10^{-22} atm, proportional to $P_{O_2}^{-1/4}$ for the oxygen pressure range 10^{-8}–10^{-15} atm and proportional to $P_{O_2}^{-1/4}$ for the oxygen pressure range greater than 10^{-4} atm. The region of linearity where the electrical conductivity varies as $-\frac{1}{4}$th power of P_{O_2} increased as the temperature was decreased. The observed data are consistent with the presence of small amounts of acceptor impurities in $CaTiO_3$. The band-gap energy (extrapolated to zero temperature) was estimated to be 3.46 eV.