JOURNAL OF SOLID STATE CHEMISTRY 33, 273–276 (1980)

Abstracts of Forthcoming Articles

Crystal Structure and Mössbauer Measurements of Monoclinic Sodium Hexacyanoferrate(III) Dihydrate. T. KATILA, M. LESKELÄ, L. NIINISTÖ,* K. J. RISKI, J. VALKONEN, AND J. YLÄ-JÄÄSKI, Department of Chemistry, Helsinki University of Technology, SF-02150 Espoo 15, Finland. The crystal structure of monoclinic sodium hexacyanoferrate(III) dihydrate has been solved from single crystal data. $Na_3Fe(CN)_6 \cdot 2H_2O$ crystallizes in the space group $C2/m$ with a = 13.551(8), b = 7.482(4), c = 6.515(4) Å, β = 106.12(5)° and two formula units in the cell. The structure was refined to an R-value of 0.035 based on 857 observed reflections. The structure consists of layers formed by distorted sodium coordination octahedra, which are joined together by common edges or faces. These layers are connected together by regular $Fe(CN)_6$ octahedra. Mössbauer spectra of ^{57}Fe in $Na_3Fe(CN)_6 \cdot 2H_2O$ have been measured in the temperature range 0.04–300 K, utilizing a dilution refrigerator for cooling. A magnetic transition was observed at 0.31 K and above this temperature a quadrupole doublet was obtained with $e^2qQ/2 = 0.669(2)$ mm/sec (at 300 K). Well below the magnetic transition temperature two six-line patterns were observed with effective magnetic fields 26.3 and 23.4 T.

The "Grain-Boundary Effect" in Doped Ceria Solid Electrolytes. DA YU WANG AND A. S. NOWICK*, Henry Krumb School of Mines, Columbia University, New York, New York 10027. The ac electrical behavior of sintered polycrystalline $CeO_2:CaO$ and $CeO_2:Y_2O_3$ solid electrolytes is studied. Complex impedance plots show the presence of an extra arc due to the presence of relatively high-resistivity material along the grain boundaries. This "Grain-boundary effect" is greatest for dilute solid solutions and "pure" samples and becomes vanishingly small for dopant concentrations $\gtrsim 15$ mole%. The effect can also be reduced by shortening the sintering time. The activation enthalpy for the grain-boundary conductivity is substantially higher than that of the lattice conductivity, especially at low dopant levels. This fact eliminates the Bauerle constriction model. The results suggest that the effective dopant concentration near the grain boundaries may be substantially reduced from the bulk value.

Studies on the Compounds in Ba–Fe–S System. II. Disordered Intergrowth Structure in $Ba_3Fe_{1+x}S_5$ ($\frac{1}{3} \leq x \leq \frac{2}{5}$) Observed by Electron Microscopy. N. NAKAYAMA,* K. KOSUGE, AND S. KACHI, Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan. Shattered crystallites of $Ba_2Fe_{1+x}S_5$ ($\frac{1}{3} \leq x \leq \frac{2}{5}$) were examined by electron microscopy. Both β-$Ba_9Fe_4S_{15}$ (x = 0.333) and $Ba_{15}Fe_7S_{25}$ (x = 0.40), previously reported members of $Ba_{3p}Fe_qS_{5q}$ series, were identified by electron diffraction patterns, and supercell periodicities, 25.5 Å ($\simeq 3a_0$) and 42.0 Å ($\simeq 5a_0$), respectively, were resolved as lattice fringes. Some crystals with intermediate compositions showed electron diffraction patterns with diffuse superlattice reflections. Their lattice fringe patterns showed a microscopic disordered intergrowth structure consisting of three periodicities, $3a_0$, $5a_0$, and $4a_0$. The intergrowth structure is a disordered one and can be analyzed based on the one-dimensional disorder model of Fe occupation in the hexagonal rings of the Ba_3S_5 framework. It is also characteristic of the "microsyntactic" intergrowth.

An Investigation of the Structure of $12HBaCoO_{2.6}$ by Electron Microscopy and Powder Neutron Diffraction. A. J. JACOBSON* AND J. L. HUTCHISON, Exxon Research and Engineering Company, P.O. Box 45, Linden, New Jersey 03104. A combination of high-resolution electron microscopy and profile analysis of powder neutron data have been used to determine the structure of the perovskite-related phase $12HBaCoO_{2.6}$. The structure is based on a 12-layer stacking sequence $(ccchhh)_2$ (space group $P6_3/mmc$). The oxygen vacancies were found to be nonrandom and are introduced by the replacement of some BaO_3 layers by BaO_2 layers of the type found in $Ba_3V_2O_8$.

Etude du Pouvoir Thermoelectrique des Composes $Cr_3Se_{4-x}Te_x$ ($0 \leq x \leq 4$). G. PEIX, D. BABOT, AND M. CHEVRETON*, Laboratoire d'Etude des Matériaux, ERA 602, Batiment 303, INSA, 20, avenue Albert-Einstein, 69621 Villeurbanne Cédex, France. Seebeck coefficient (S) determination has been carried out on nine polycrystalline samples in the $Cr_3Se_{4-x}Te_x$ series (x =

0; 0.5; 1; 1.5; 2; 2.5; 3; 3.5; 4). A thermoelectric cell was constructed, which works automatically between 14 and 320 K with a precision better than 5%. For high concentrations in selenium, the thermoelectric power remains negative over the whole temperature range. Such is not the case with tellurium-rich compounds where the Seebeck coefficient, negative at 320 K, becomes positive at lower temperatures. Anomalies are observed on the $S = f(T)$ curves at temperatures T_t in the vicinity of the magnetic transitions. Transport properties for selenium-rich compounds are discussed in terms of narrow-band conduction. Hole conduction, which appears for $x \geq 3$ at low temperature, is interpreted as due to an overlapping band conduction between 3*d* levels and the valence band.

About Stannous Fluoride SnF_2. III. Thermal Expansion. G. DENES, Laboratoire de Chimie Minérale D, Université de Rennes I, 35042 Rennes Cédex, France. The unit cell parameters of SnF_2 were measured from −200 to 190°C. The tensor of thermal expansion of the three phases (α, β, and γ) was computed from the expansion in each $(h\ k\ l)$ direction by a least-squares method. The thermal expansion of each phase is related to its crystal structure and physical properties (molecular structure of α-SnF_2, ferroelastic properties of the β-phase).

Phase Equilibria of the Oxide–Hydroxide–Halide Systems of Sm, Eu, and Gd. The Crystal Structure of $Gd_3O(OH)_5Br_2$. EDWARD T. LANCE-GOMEZ* AND JOHN M. HASCHKE, Procter and Gamble Company, Winton Hill Technical Centers, 6060 Center Hill Road, Cincinnati, Ohio 45224. An investigation of hydrothermal phase equilibria in the halide-containing (Cl, Br, I) systems of Sm, Eu, and Gd has shown that diversities in behavior occur across the lanthanide (*Ln*) series and within the halide group. In the chloride systems, the trihydroxide, two phases at a Cl/*Ln* ratio of 0.4 and $Ln(OH)_2Cl$ phases are found. Equilibria in the bromide systems are more complex; $Ln(OH)_3$, $Ln_7(OH)_{18}Br_3$, a high-temperature phase at Br/*Ln* = 0.45, $Ln_3O(OH)_5Br_2$, and $Ln(OH)_2Br$ are observed. A single iodide-containing phase, $Ln(OH)_{2.67}I_{0.33}$ is found. X-Ray diffraction data are reported for all the previously unreported phases and the thermal decomposition behavior of representative phases is described. The results of a single crystal X-ray structure determination of orthorhombic (*Pmmn*) $Gd_2O(OH)_5Br_2$ are reported and discussed.

Neutron Powder Diffraction and Magnetic Measurements on $CsMnI_3$. H. W. ZANDBERGEN, Gorlaeus Laboratories, University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands. Results of neutron powder diffraction and magnetic measurements on single crystals of $CsMnI_3$ are reported. Three-dimensional ordering takes places at $T_c = 11.1(3)$ K. Above T_c very broad peaks occur in the neutron powder diffraction diagram, indicating one-dimensional correlations along the chain. Below T_c the Mn^{2+} ions are coupled antiferromagnetically along the chain. Interchain exchange leads to a 120° structure, slightly distorted due to anisotropy. One-third of the chains have their magnetic moment parallel to the *c* axis and the rest of the chains have magnetic moments making an angle of 50(2)° with the *c* axis. The magnetic moment as found from neutron diffraction extrapolated to 0 K is 3.7(1) μ_B, indicating a considerable zero-point spin reduction. The intrachain exchange J/k was found to be −9.1(1) K, whereas the ratio of the inter- to intrachain interaction was determined as $|J'/J| = 5 \times 10^{-3}$. A spin flop occurs at $H = 54$ kOe on application of a magnetic field parallel to the *x* axis. When a field perpendicular to the *c* axis is applied a spin reorientation occurs at 1 kOe.

Phase Transition in the Family $La_xBi_{4-x}Ti_3O_{12}$ in Relation to Lattice Symmetry and Distortion. MASAJI SHIMAZU*, JUNZO TANAKA, KUNITAKA MURAMATSU, AND MASAYUKI TSUKIOKA, National Institute for Research in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki 305, Japan. The ferroelectric phase transition in the family $La_xBi_{4-x}Ti_3O_{12}$ was investigated by X-ray diffractometry and differential scanning calorimetry. The crystal symmetry is orthorhombic in the range $1 > x \geq 0$ and tetragonal in $x \gtrsim 1$. It was found that the shift of the phase transition temperature is closely related to crystallographic symmetry and lattice distortion. (1) As the value of *x* increases, the ratio of lattice parameters, a/b, decreases toward 1. (2) In the range $1 > x \gtrsim 0$, the lattice distortion increases with increase of *x*; just before x exceeds about 1, the distortion reaches a maximum. (3) As *x* exceeds about 1, the distortion decreases distinctively. (4) In the orthorhomic region, the phase-transition temperature decreases with increase of *x*. (5) In the tetragonal region, the transition does not occur. (6) The relation of transition temperature *T* to *x* is represented by a nonlinear function.

Heat Capacity Measurements of $Mn_xFe_{3-x}O_4$. KEIJI NAITO*, HIDEAKI INABA, AND HARUYOSHI YAGI, Department of Nuclear Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya,