

## Abstracts of Forthcoming Articles

*A Study of the MgO–V<sub>2</sub>O<sub>5</sub> System.* G. M. CLARK AND R. MORLEY, Department of Applied Chemical and Biological Sciences, The Polytechnic, Huddersfield HD1 3DH, England. An investigation was made of solid–solid reactions in MgO/V<sub>2</sub>O<sub>5</sub> mixtures of various stoichiometries. Three compounds were obtained, viz. Mg<sub>3</sub>V<sub>2</sub>O<sub>8</sub>, Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub>, and MgV<sub>2</sub>O<sub>6</sub>; no evidence was obtained to indicate formation of other MgO–V<sub>2</sub>O<sub>5</sub> compounds reported in the literature. DTA data are listed for the three compounds and some observations are made on the mechanism of formation of the compounds. A new polymorph of Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub> was prepared and its space group and cell parameters were deduced from the X-ray powder diffraction pattern. This polymorph undergoes a transition, reversible with difficulty, at 980–990°K.

*Structure Cristalline des Hydroxytellurites de Nickel et de Cobalt.* G. PEREZ AND F. LASSERRE, Lab de Chimie Minerale Structurale, 6 blvd de Broglie, 76130 Mont Saint Aignan, France AND J. MORET AND M. MAURIN, Lab de Chimie Minerale C, Universite des Sciences et Techniques du Languedoc, 34060 Montpellier, France. The hydroxytellurites of nickel and cobalt crystallize in the hexagonal system. Parameters are  $a = 12.693$ ,  $c = 4.958$  Å and  $a = 13.034$ ,  $c = 5.016$  Å, respectively. The space group is  $P6_3mc$  ( $C_{6v}^4$ ). The Ni and Co atoms are located in oxygen octahedra sharing common faces. The chains of octahedra are joined to each other through corner sharing and are disposed about the sixfold axis. The tellurium atoms are placed above an equilateral triangle formed by three oxygen atoms.

*Etude Cristallographique et Magnetique d'Oxydes Mixtes de Formule Ba<sub>3</sub>Fe<sub>2-x</sub>Y<sub>x</sub>UO<sub>9</sub>.* J. C. GRENET AND P. POIX, Lab de Chimie Minerale Bat. 420, Universite de Paris-Sud, 91400 Orsay, France. Crystallographic study of the title compounds ( $0.2 \leq x \leq 1.2$ ) shows that they are perovskite-type compounds of probable space group  $Fm\bar{3}m$  with ordering between  $4a$  and  $4b$  sites. The  $8c$  sites contain the Y<sup>3+</sup> ions. The compounds show ferrimagnetic properties. For each composition, the distribution of ions in the different crystallographic sites is given.

*Etude a Haute Temperature des Systemes Formes par le Sesquioxyde de Lanthane et les Sesquioxides de Lanthanides. I. Diagrammes de Phases (1400°C < T < T Liquide).* J. COUTURES, A. ROUANET, R. VERGES, AND M. FOEX, Lab des Ultra-Refractaires, 66120 Odeillo-Fontromeu, France. Studies involving thermal and X-ray diffraction analyses have been carried out at high temperature on the systems La<sub>2</sub>O<sub>3</sub>–Ln<sub>2</sub>O<sub>3</sub> (Ln = lanthanon element). Homogeneity and thermal stability of cubic (Tl<sub>2</sub>O<sub>3</sub> form), monoclinic (Sm<sub>2</sub>O<sub>3</sub> form), hexagonal  $A$  or  $H$  (La<sub>2</sub>O<sub>3</sub> form), and cubic  $X$  solutions have been examined. Tentative equilibrium diagrams have been drawn from 1400°C through the liquid state.

*High Temperature Rutile-Derived Crystallographic Shear Structures. I. (020)<sub>r</sub> CS Structures.* L. A. BURSILL, Physics Department, University of Melbourne. I. E. GREY, CSIRO Division of Mineral Chemistry, P.O. Box 124, Port Melbourne. AND D. J. LLOYD, Chemistry Department, University of Melbourne, Parkville, Victoria 3052, Australia. Electron diffraction and single crystal X-ray diffraction techniques have been applied to a study of the structures of phases in the Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> system, for compositions in the range 14–16 wt% Fe<sub>2</sub>O<sub>3</sub> and for temperatures above 1450°C. The compounds in this system may be described as (020)<sub>r</sub> CS phases in which adjacent rutile slabs, infinitely extended along [100]<sub>r</sub> and [001]<sub>r</sub>, are displaced by  $\frac{1}{2}$ [011]<sub>r</sub> across (020)<sub>r</sub> CS planes. In the CS planes, about two-thirds of the available metal-atom octahedral sites are occupied in a deficient NiAs arrangement. The composition range studied is spanned by a continuous series of (020)<sub>r</sub> intergrowths formed by the ordered mixing of structures with two different CS plane spacings, namely  $9 \times d_{(020)r}$  and  $11 \times d_{(020)r}$ . Conventional structure solution methods could not be applied to these infinitely adaptive structures because of the small intensity data to parameter ratios for the high-order intergrowths. We describe a method of structure solution based on a series of successive approximations. The method was applied to determine

the structure of one of the intergrowths using single crystal X-ray diffraction data. For the temperature range studied the CS phases are within a few degrees of their melting points, and this is reflected in a departure from complete structural order. The results show both long-range disorder in the intergrowth sequences and also an absence of correlation between the metal atom ordering in one CS plane and the next. This disorder is manifested by diffuse scattering in the diffraction patterns. The (020), CS structures transform reversibly to the well-known (121)<sub>r</sub>-(132)<sub>r</sub> family of ordered rutile CS structures below 1450°C.

*Magnetic Susceptibility of Single Crystal Fe<sub>1-x</sub>S.* J. L. HORWOOD, M. G. TOWNSEND, AND A. H. WEBSTER, Mineral Sciences Laboratories, Canada Centre for Mineral and Energy Technology, Ottawa, Canada K1A 0G1. Stoichiometric FeS is characterized by three phase transitions, one structural at  $T_\alpha$  and the others magnetic at  $T_s$  and  $T_N$ . We have obtained magnetic susceptibility data in the temperature range 80° to 600°K on single crystals of several compositions of Fe<sub>1-x</sub>S for  $0 \leq x \leq 0.07$ . The magnetic susceptibilities of very nearly stoichiometric FeS show the two transitions well separated [ $T_\alpha = 420^\circ\text{K}$ ,  $T_s = 445^\circ\text{K}$ ]. In the region of  $T_s$ , the spins do not rotate gradually with temperature but flip locally due to a small spread in composition. By comparing the data with that of NiS we infer that FeS is a localized spin antiferromagnet in contrast to NiS, which is generally considered to be an itinerant antiferromagnet.  $T_s(x)$  decreases linearly with increasing metal deficiency. This dependence can be partly accounted for by a decrease in the spin-orbit coupling energy arising from increasing covalency; however, we conclude that a concomitant increase in magnetocrystalline anisotropy energy also occurs in this range.

*Mossbauer Effect in Single Crystal Fe<sub>1-x</sub>S.* J. R. GOSSELIN, M. G. TOWNSEND, R. J. TREMBLAY, AND A. H. WEBSTER, Mineral Sciences Laboratory, Canada Centre for Mineral and Energy Technology, Ottawa, Canada K1A 0G1. Mossbauer spectra have been recorded for single crystals of very nearly stoichiometric FeS and Fe<sub>0.93</sub>S at temperatures between 80° and 600°K. The spectra of nearly stoichiometric FeS indicate that the low-temperature 2C structure with spins  $\parallel c$  preserves the spin orientation  $\parallel c$  during the structural transformation to 1C at  $T_\alpha (= 420^\circ\text{K})$ . However, because of a miscibility gap, a few percent of the high-temperature 1C structure with spins  $\perp c$  is present even at 300°K and the concentration of this component increases with temperature. At  $T_s (= 445^\circ\text{K})$  the spins in the 1C structure that are  $\parallel c$  rotate  $\perp c$ . In Fe<sub>0.93</sub>S, the hyperfine splittings indicate that the rotation of the spins from  $\parallel c$  to  $\perp c$  at 170°K is a first-order process.

*Zur Kristallstruktur von FeI<sub>3</sub>O<sub>9</sub>.* M. JANSEN, Institut für Anorganische und Analytische Chemie der Justus Liebig-Universität, 63 Giessen, Sudanlage, Germany. Single crystals of FeI<sub>3</sub>O<sub>9</sub> were obtained by oxidizing FeI<sub>2</sub> at 520°C and 500 atm oxygen pressure. The crystal structure has been determined and refined by full matrix least-squares procedures using diffractometer data to a final  $R$ -value of 0.067; the space group is  $P6_3-C_6^6$ ,  $a = 9.225 \text{ \AA}$ ,  $c = 5.224 \text{ \AA}$ ,  $c/a = 0.57$ . The structure consists of FeO<sub>6</sub>-octahedra connected by iodine, each of which is coordinated by three oxygen [ $d(\text{I}-\text{O})$ ; 1.89 and 1.90 Å for bridging O; 1.79 Å for terminal O]. The Cr and  $\beta$ -Sc iodates have the same structure.

*Phase Equilibria in the System Fe-Fe<sub>2</sub>O<sub>3</sub>-Lu<sub>2</sub>O<sub>3</sub> at 1200°C.* T. SEKINE AND T. KATSURA, Department of Chemistry, Tokyo Institute of Technology, Tokyo 152, Japan. Phase equilibria in the title system have been established at 1200°C. The following phases were stable: lutetium sesquioxide, hematite, magnetite, wustite, metallic iron, lutetium-iron-perovskite, lutetium-iron-garnet, LuFe<sub>2</sub>O<sub>4</sub>, and Lu<sub>2</sub>Fe<sub>3</sub>O<sub>7</sub>. The standard free energy of formation from metallic iron, Lu<sub>2</sub>O<sub>3</sub>, and oxygen at 1200°C of LuFe<sub>2</sub>O<sub>4</sub>, Lu<sub>2</sub>Fe<sub>3</sub>O<sub>7</sub>, LuFeO<sub>3</sub>, and Lu<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> has been determined to be  $-100.3 \pm 0.2$ ,  $-158.2 \pm 0.2$ ,  $-57.5 \pm 0.3$ , and  $-279.1 \pm 0.9$  kcal/mole, respectively.

*Preparation, Phase Equilibria, and Crystal Chemistry of Lanthanum, Praseodymium, and Neodymium Hydroxide Chlorides.* E. T. LANCE AND J. M. HASCHKE, Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104. The preparation of hydroxide chlorides of lanthanum, praseodymium, and neodymium has been achieved by hydrothermal methods at 550°C and 1530 atm. Three phases [Ln(OH)<sub>3</sub>, Ln(OH)<sub>2.55</sub>Cl<sub>0.45</sub>, and Ln(OH)<sub>2</sub>Cl] have been characterized by analytical and X-ray methods. The observed compositions are closely defined by the  $x = 0, 0.5$ , and 1 members of the hom-