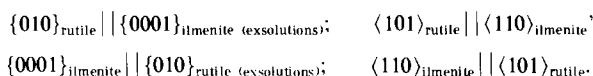


Abstracts of Forthcoming Articles

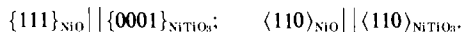
Dimorphisme du Disulfure de Lanthane LaS₂. SIMONE BENAZETH, MICHELINE GUITTARD, AND JEAN FLAHAUT, Laboratoire de Chimie Minérale Structurale, Faculté des Sciences Pharmaceutiques et Biologiques de Paris V, 4, avenue de l'Observatoire, 75270 Paris Cédex 06, France. The stoichiometric lanthanum disulfide LaS₂ presents a reversible phase transition at about 750°C. The α low-temperature form is monoclinic with the LaSe₂ type of structure. All the crystals are twinned with the same twin law (100). The cell parameters are $a = 8.18$; $b = 8.13$; $c = 4.03$ Å; $\gamma = 90^\circ$, space group $P2_1/a$. The β high-temperature form has the orthorhombic structure previously described with the parameters $a = 8.13$; $b = 16.34$; $c = 4.14$ Å, space group $Pnma$. The two structures are compared.

The Structure of Quartz at 25 and 590°C Determined by Neutron Diffraction. A. F. WRIGHT AND M. S. LEHMANN, Institut Laue Langevin, 156X, 38042 Grenoble Cédex, France. Analysis of single-crystal data on the α to β transformation in quartz, which takes place at 573°C, showed that the model which, until now, has best agreed with available X-ray data does not hold for the neutron data. In the earlier model both oxygen and silicon atoms move to special positions (6j and 3c in the space group $P6_22$). The new data for β -quartz were best explained by assuming a disorder for the oxygen atom around the 6j position, and in order to keep regular SiO₄ tetrahedra, a corresponding small disorder in the silicon atom is assumed.

Phase Relations and Exsolution Phenomena in the System NiO-TiO₂. THOMAS ARMBRUSTER, Institut für Mineralogie der Ruhr-Universität, D-4630, Bochum, West Germany. The phase relations in the system NiO-TiO₂ were studied between 1000 and 1600°C using quenched powder specimens, DTA runs, and single-crystal diffusion couples. Quenching experiments establish the stable phases TiO₂ (rutile), NiTiO₃, an ilmenite structure type, Ni_{2(1+x)Ti_{1-x}O₄} ($x > 0.16$), a cation-excess spinel, and Ni_{1-2x}Ti_xO (rock salt structure type). DTA runs reveal the existence of an additional nonstoichiometric ilmenite phase Ni_{1-2x}Ti_{1+x}O₃ ($x < 0.03$) above 1260°C. In quenched (1500°C, 1450°C) or slowly cooled single-crystal diffusion couples, mutual oriented exsolutions occur in the rutile guest crystal and in the ilmenite diffusion zone. Orientation relations are:



The cation-excess spinel decomposes below 1375°C into oriented intergrowth of NiTiO₃ (ilmenite) and NiO:



Mise en Evidence de l'Entité Sb₂F₄O dans un Composé d'Addition Moléculaire avec l'Urée: Etude Structurale de ((NH₂)₂CO)₂ · Sb₂F₄O. M. BOURGAULT, R. FOURCADE, AND G. MASCHERPA, Laboratoire de Chimie Minérale D, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 Montpellier Cédex, France. The X-ray structure determination of |(NH₂)₂CO|₂ · Sb₂F₄O shows the existence of linked units urea-Sb₂F₄O which show the Sb₂F₄O entity, not yet known. Crystal structure was solved with a single-crystal X-ray diffraction study (the final R value is 0.046). The Sb₂F₄O unit is composed of a symmetric and short Sb-O-Sb bridge, and of four fluorine atoms, two being bonded to each antimony atom and situated in "trans" position relative to the Sb-O-Sb bridge. The bridge bond strength is assigned to a $p\pi d\pi$ overlap.

The Crystal and Molecular Structure of tris (ortho-Aminobenzoato)aquoyttrium(III). Y(H₂NC₆H₄COO)₃ · H₂O. SHARON M. BOUDREAU AND HELMUT M. HAENDLER, Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824. tris(ortho-Aminobenzoato)aquoyttrium(III), Y(H₂NC₆H₄COO)₃ · H₂O, crystallizes in the monoclinic space group, C2/c, with eight molecules in a unit cell of dimensions: $a = 30.89(1)$ Å, $b = 9.09(1)$ Å, $c = 14.85(1)$ Å, and $\beta =$

109.3(1)^o. The structure was determined using three-dimensional X-ray diffraction data gathered on multiple-film equi-inclination, integrated Weissenberg and precession photographs taken about two crystal axes. The structure, excluding the hydrogen atoms, was solved from Patterson and electron density maps and refined by least-squares methods to a final *R* of 0.081. The coordination about the yttrium atom is sevenfold, best described by a capped trigonal prism. Each *ortho*-aminobenzoate ligand acts as a bridging bidentate ligand, resulting in six *ortho*-aminobenzoate residues coupled to each yttrium atom. The water molecule occupies the seventh position. This bonding configuration generates a structure in which each yttrium atom in (100) is attached to two other yttrium atoms via carboxylate bridges to give parallel sets of polymeric chains coincident with (100). It is suggested that this polymeric character accounts for the extreme insolubility of $Y(H_2NC_6H_4COO)_3 \cdot H_2O$.

Self-Compensation in Niobium-Doped TiO₂. N. G. EROR, Oregon Graduate Center, Beaverton, Oregon 97005. Gravimetric measurements on pure and niobium-doped TiO₂ have shown that the reversible change of oxygen content, between specified states of oxidation and reduction, is proportional to the dopant concentration. These measurements indicate that the donor-dopants are electronically compensated by additional oxygen uptake in the oxidized state. The range of this reversible change in oxygen stoichiometry is up to more than an order of magnitude larger than the oxygen nonstoichiometry of the undoped oxides. Self-compensation has been measured in TiO₂ with donor-dopant concentrations of up to 8 atom% Nb⁺⁵ over the oxygen partial pressure range 10⁰–10⁻¹⁵ atm. For the case of Nb⁺⁵ doped TiO₂ the monoclinic phase "TiNb₂O₇" was found to exsolve under oxidizing conditions for Nb⁺⁵ concentrations >8 atom%. The exsolved phase transformed into niobium doped rutile under reducing conditions. The gravimetric measurements for Nb⁺⁵ concentrations <8 atom% can be explained by the creation of metal deficit point defects (self-compensation) or a model involving a shear structure.

Crystal Structure of the Ordered Pyrochlore NH₄Fe^{II}Fe^{III}F₆: Structural Correlations with Fe₂F₃ · 2H₂O and Its Dehydration Product Fe₂F₃ · H₂O. G. FEREY, M. LEBLANC, AND R. DE PAPE, Laboratoire des Fluorures et Oxyfluorures Ioniques, Faculté des Sciences, Route de Laval, 72017 Le Mans Cédex, France. Crystal structure of NH₄Fe^{II}Fe^{III}F₆ is studied in order to explain further its peculiar antiferromagnetic behavior compared to the spinglass one of the pyrochlore family. NH₄Fe^{II}Fe^{III}F₆ is orthorhombic, space group *Pnma* with *a* = 7.045 (4) Å, *b* = 7.454 (4) Å, *c* = 10.116 (6) Å, *Z* = 4. Diffraction data on single crystals obtained by hydrothermal synthesis, collected on an automatic four-circle diffractometer, have been refined by full-matrix least-squares calculations to a weighted value of 0.029 (unweighted *R* = 0.024) for 798 observed reflections. This structure is derived from the pyrochlore structure, with a cationic order between Fe²⁺ and Fe³⁺ ions. (Fe^{II}F₆)⁴⁻ octahedra form infinite *trans* chains along [100] by sharing corners although similar chains of (Fe^{III}F₆)³⁻ octahedra lie along [010]. This type of Fe^{II}–Fe^{III} order is related to a similar one existing in Fe₂F₃ · 2H₂O, the dehydration of which leads to the pyrochlore Fe₂F₃ · H₂O. A mechanism is proposed to explain the formation of this compound.

Crystal Growth and Electrical Properties of Lithium, Rubidium, and Cesium Molybdenum Oxide Bronzes. PIERRE STROBEL AND MARTHA GREENBLATT, Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08903. Crystals of Li_{0.33}MoO₃ (blue), Rb_{0.23}MoO₃ (blue), and Cs_{0.31}MoO₃ (red) were grown by electrolysis from MoO₃–*M*₂MoO₄ melts (*M* = alkali metal) with composition 70–77 mole% MoO₃. Melts richer in *M*₂MoO₄ produced MoO₂ only. Correlation is made between bronze formation and the coordination of Mo in the melt and in the equilibrium solid phase *M*₂Mo₄O₁₃. Li_{0.33}MoO₃ and Cs_{0.31}MoO₃ are semiconductors with high-temperature range activation energies 0.16 and 0.12 eV. Rb_{0.23}MoO₃ has an electrical behavior similar to that of blue K_{*x*}MoO₃ with a semiconductor–metal transition at (170 ± 5) K. ESR spectra observed in Li_{0.33}MoO₃ and Rb_{0.23}MoO₃ single crystals at 4.2 K show extensive delocalization of the 4*d* electron associated with Mo(V) centers. Attempts to grow molybdenum bronzes containing Ca or Y were unsuccessful.

Synthesis of Rare Earth Monoxides. I. M. LEGER, N. YACOUBI, AND J. LORIER, E. R. 211, 1 place A. Briand, 92190 Meudon, France. The standard Gibbs energy changes for the formation of an ionic or metallic monoxide from rare earth metal and sesquioxide have been calculated. Under high pressures ionic ytterbium monoxide and lighter rare earth metallic monoxides should be obtained which is