

The series of compounds  $R\text{TiO}_3$ ,  $R = \text{Gd, Tb, Dy, Ho, Er, and Tm}$ , were obtained as single-phase materials via solid state reaction between  $\text{Ti}_2\text{O}_3$  and  $R_2\text{O}_3$  at ca.  $1500^\circ\text{C}$  in welded molybdenum crucibles under argon.  $\text{YbTiO}_3$  and  $\text{LuTiO}_3$  could not be obtained as single-phase materials using this procedure. Lattice constants for all compounds were determined from powder X-ray data and are compared with previous results. All of these materials order magnetically between 30 and  $70^\circ\text{K}$ . From the appearance of the  $\chi_m^{-1}$  vs  $T$  curve the type of order can be identified as ferrimagnetic. High-temperature susceptibility data have been fitted to a two-sublattice molecular field model and the intra- and intersublattice interaction constants have been extracted. It is found that the Ti-Ti interaction is ferromagnetic and relatively constant from  $R = \text{Gd}$  to  $R = \text{Lu}$ . Low-temperature magnetization-field data suggest the existence of complex magnetic structures or large magnetocrystalline anisotropy or both. The magnetic properties of the  $R\text{TiO}_3$  series are compared to those of the chemically similar and better-known  $R\text{MO}_3$  phases where  $M = \text{Al, V, Cr, Mn, and Fe}$ . The observed differences are shown to follow from the sign of the  $M$ - $M$  interaction, which is ferromagnetic for  $M = \text{Ti}$  and antiferromagnetic for  $M = \text{V, Cr, Mn, and Fe}$ , together with the implications of the crystal symmetry for the  $R$ - $M$  interaction.

*Thermodynamics of Hydrogen Trapping in Intermetallic Compounds: Application to  $\text{LaNi}_5/\text{H}$ .* TED B. FLANAGAN, C. A. WULFF, AND B. S. BOWERMAN. Department of Chemistry, University of Vermont, Burlington, Vermont 05405.

It has been observed for several intermetallic compound/H systems that deviations from Sieverts' law of ideal solubility occur which are in the opposite direction from the deviations from ideality which occur in pure metal/H systems. The principal source of nonideality in both types of interstitial solutions arises from the changes of the relative partial molar enthalpy of  $\text{H}_2$  solution,  $\Delta H_{\text{H}}$ , with H content. The variations of  $\Delta H_{\text{H}}$  with H content are, however, in the opposite directions for intermetallic- and pure metal/H interstitial solutions. Relative partial molar entropies for solution of  $\text{H}_2$  in the  $\alpha$ -phase of the  $\text{LaNi}_5/\text{H}$  system are given at  $298.2^\circ\text{K}$ . These have been determined from calorimetric determinations of  $\Delta H_{\text{H}}$  and measurements of  $\Delta G_{\text{H}}$  ( $= RT \ln p_{\text{H}_2}^{1/2}$ ). The partial entropies show unusual extrema as a function of H content. A model based on trapping of H atoms is proposed which explains the variations of  $\Delta H_{\text{H}}$  and  $\Delta S_{\text{H}}$ . Since the deviations from ideality arising from an increase of  $\Delta H_{\text{H}}$  with H content seem to be limited to solids with at least two different ordered metal components, e.g., intermetallic compounds, it seems reasonable to assign the trapping sites to interstices which result from an interchange of metal atoms. This interchange may create interstices rich in those nearest-neighbor metal atoms which have the greatest affinity for H.

*Lead Phosphate Apatites Substituted by Rare Earth, Sodium, and Potassium Ions.* I. MAYER, A. SEMADJA, AND V. WEISS. Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel.

Rare-earth-substituted lead apatites of the  $\text{Pb}_{10-2x}\text{Ln}_x\text{M}_x(\text{PO}_4)_6\text{Y}_2$  ( $\text{Ln} = \text{La, Nd, Eu, Gd, Dy, and Y}$ ;  $M = \text{Na and K}$ ;  $Y = \text{F and Cl}$ ) systems were prepared and studied by X-ray diffraction and infrared methods. The powder patterns of all the compounds show the apatite-like hexagonal structure. Single-crystal precession data reveal that the space group of the  $\text{Pb}_6\text{Ln}_2(\text{PO}_4)_6\text{F}_2$  compounds is probably  $P\bar{6}$  while that of  $\text{Pb}_6\text{Ln}_2\text{K}_2(\text{PO}_4)_6\text{F}_2$  is  $P6_3/m$ . Analysis of the spectra of substituted Ca, Ba, and Pb compounds shows the effect of substituted ions on the spectra and supports the assumption that substitution in the Ba and Pb systems is an ordered process. Ordering of the substituted ions in the systems studied is discussed in view of changes in lattice parameters, size conditions, and polarizing properties of the ions.

*Neutron Diffraction Study on the Mechanism of the Topotactic Reduction of  $2\text{H-TaS}_2$  Electrodes.* C. RIEKEL, H. G. REZNIK, AND R. SCHÖLLHORN. Anorganisch-chemisches Institut der Universität, Gievenbecker Weg 9, 4400 Münster, West Germany.

The dynamic investigation by neutron diffraction of the topotactic reduction of  $2\text{H-TaS}_2$  electrodes in  $\text{K}^+/\text{D}_2\text{O}$  electrolyte to the ionic layered hydrate  $\text{K}_{0.5}^+(\text{D}_2\text{O})_{0.5}[\text{TaS}_2]^{0.5-}$  is shown to proceed via third-stage  $\text{K}_x^+(\text{D}_2\text{O})_y[\text{TaS}_2]_3^{x-}$ , second-stage  $\text{K}_x^+(\text{D}_2\text{O})_y[\text{TaS}_2]_2^{x-}$ , and first-stage  $\text{K}_x^+(\text{D}_2\text{O})_y[\text{TaS}_2]^{x-}$  intermediates. A comparative study by X-ray diffraction on the cathodic intercalation of  $2\text{H-TaS}_2$  and

2H-NbS<sub>2</sub> electrodes with hydrated main group and transition metal ions reveals analogous behavior; the formation of higher-stage intermediates is supposedly correlated with stable electronic layer states. Influence of kinetic factors is observed for larger guest cations such as transition metal complexes and organic ions. CdI<sub>2</sub>-type host lattices with an octahedral environment of intralayer cations show different reaction pathways, although the occurrence of intermediate states (at least in the nucleation phase) can be demonstrated. It is concluded that the presence of ordered intermediate states is a general phenomenon in topotactic electrode processes of layered dichalcogenides.

*Electronic Properties of Semiconducting Cd<sub>2</sub>GeO<sub>4</sub>.* E. R. WHIPPLE, S. N. SUBBARAO, AND F. P. KOFFYBERG. Department of Physics, Brock University, St. Catharines, Ontario L2S 3A1, Canada.

Cd<sub>2</sub>GeO<sub>4</sub> has been prepared from CdO and GeO<sub>2</sub> by solid state reaction at 850°C as a low-resistivity ( $\rho = 1 \Omega\text{-cm}$ ) *n*-type semiconductor. Its conductivity is increased by doping with trivalent metal ions and decreased by heating in oxygen. The electrons originate from shallow donors and their mobility is determined by a combination of large polaron formation and impurity scattering. From photoelectrolysis data the band gap is determined to be indirect, at 3.15 eV; the first direct transition occurs at 4.1 eV. The relations among conditions of preparation, defect structure, and carrier concentration have been examined, but the available data do not allow an unambiguous identification of the nature of the donor center.

*Über geordnete Perowskite mit Kationenfehlstellen. V. Verbindungen der Zusammensetzung A<sup>2+</sup>B<sup>3+</sup>U<sup>6+</sup>□<sub>1/6</sub>O<sub>6</sub>.* G. RAUSER UND S. KEMMLER-SACK. Institut für Anorganische Chemie der Universität Tübingen Aug der Morgenstelle 18, D-7400 Tübingen, Germany.

Ordered perovskites with octahedral vacancies could be obtained for a new series of composition A<sup>2+</sup><sub>12</sub>B<sup>3+</sup><sub>6</sub>M<sup>6+</sup><sub>5</sub>□O<sub>36</sub> ≡ A<sup>2+</sup><sub>2</sub>B<sup>3+</sup><sub>3</sub>M<sup>6+</sup><sub>5/6</sub>□<sub>1/6</sub>O<sub>6</sub> for M<sup>6+</sup> = U and A<sup>2+</sup> = Ba; B<sup>3+</sup> = Sm-Lu, Sc, Y, or A<sup>2+</sup> = Sr; B<sup>3+</sup> = Yb, Lu. With the exception of the cubic 1 : 1 ordered Ba<sub>12</sub>Sc<sub>6</sub>U<sub>5</sub>□O<sub>36</sub> the perovskites crystallize in distorted orthorhombic structures. For the type A<sup>2+</sup><sub>12</sub>B<sup>3+</sup><sub>6</sub>M<sup>6+</sup><sub>5</sub>□O<sub>36</sub> the cation/vacancy ratio (for the octahedral sites) is 11 : 1. This value integrates into the scheme of perovskites with octahedral vacancies and cubic stacking of the AO<sub>3</sub> sheets, where compounds with cation/vacancy ratios of 5 : 1, 7 : 1, 9 : 1, and 15 : 1 are already known.

*Preparation and Characterization of Compounds of the System Fe(Sb<sub>1-x</sub>Te<sub>x</sub>)<sub>2</sub> (0 ≤ x ≤ 1.0).* G. YAMAGUCHI, M. SHIMADA, M. KOIZUMI, AND F. KANAMARU. The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan.

The complete solid solution of Fe(Sb<sub>1-x</sub>Te<sub>x</sub>)<sub>2</sub> with the marcasite structure was synthesized. Electrical and magnetic measurements showed that the substitution of tellurium for antimony in the diamagnetic semiconductor FeSb<sub>2</sub> resulted in metallic and paramagnetic behavior in the composition range 0.1 ≤ x ≤ 0.3, but in 0.4 ≤ x ≤ 0.6 the products belonged to the arsenopyrite structure and were diamagnetic and semiconductive. The samples whose compositions were in the range 0.7 ≤ x ≤ 1.0 were semiconductors. Mössbauer effect measurements showed that isomer shift did not change, but the quadrupole splitting changed significantly from 1.28 mm/sec for FeSb<sub>2</sub> to 0.50 mm/sec for FeTe<sub>2</sub> in this solid solution.

*Electrical Transport Properties of a Nonstoichiometric Rare Earth Sulfide, EuGd<sub>2</sub>S<sub>4</sub>.* MINEO SATO, GIN-YA ADACHI, AND JIRO SHIOKAWA. Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-kami, Suita-shi, Osaka-fu, 565 Japan.

The electrical transport properties of nonstoichiometric EuGd<sub>2</sub>S<sub>4</sub> prepared by heating under a high vacuum have been investigated. The samples heated were classified into two groups on the basis of their electrical transport behavior. One group consisted of semiconducting materials heated at 1500 and 1600°C, for which the transport mechanism was found to be via electron hopping with activation energies ranging from 0.03 to 0.027 eV. Another group consisted of metallic materials heated at 1700 and 1800°C. Their electrical transport was carried out through ordinary band conduction over the measured temperature range except at temperatures lower than 120°K, where hopping with a very small activation energy (~0.0035 eV) occurred predominantly.