

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_i 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 3d levels and the valence band.

About Stannous Fluoride SnF₂, III. Thermal Expansion. G. DENES, Laboratoire de Chimie Minérale D, Université de Rennes I, 35042 Rennes Cédex, France. The unit cell parameters of SnF₂ 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 -SnF₂, ferroelastic properties of the β -phase).

Phase Equilibria of the Oxide-Hydroxide-Halide Systems of Sm, Eu, and Gd. The Crystal Structure of Gd₂O(OH)₅Br₂. 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, Ln₂(OH)₁₈Br₃, a high-temperature phase at Br/Ln = 0.45, Ln₂O(OH)₅Br₂, 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 ($Pmmn$) Gd₂O(OH)₅Br₂ are reported and discussed.

Neutron Powder Diffraction and Magnetic Measurements on CsMnI₃. 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 CsMnI₃ are reported. Three-dimensional ordering takes place 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 Mn²⁺ 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}Ti₃O₁₂ 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}Ti₃O₁₂ 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 $x \geq 1$. 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 $1 > x \geq 0$, 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 distinctly. (4) In the orthorhombic 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 Mn₂Fe_{3-x}O₄. KEIJI NAITO*, HIDEAKI INABA, AND HARUYOSHI YAGI, Department of Nuclear Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya,

Japan. Heat capacities of $Mn_xFe_{3-x}O_4$ with the composition $x = 1.0, 1.5,$ and 2.0 were measured from 200 to 740 K. λ -Type heat capacity anomalies due to ferri-paramagnetic transition were observed for all the compositions. The transition temperatures were $577, 471,$ and 385 K for the compositions $x = 1.0, 1.5,$ and $2.0,$ respectively, which are in good agreement with the results of magnetic measurements. The difference in heat capacities between the different samples was small except for the temperature range of the transition. The magnetic contribution of the observed heat capacity was obtained by assuming that the heat capacity can be expressed by the sum of the lattice heat capacity $C_l,$ the dilation contribution $C(d)$ and the magnetic contribution $C(m).$ Entropy changes due to the transition were obtained from $C(m)$ as $55.5, 50.7,$ and 49.2 J K⁻¹ mole⁻¹ for the compositions $x = 1.0, 1.5,$ and $2.0,$ respectively. The entropy changes were also calculated by assuming randomization of unpaired electron spins on each ion, but they were from 6 to 10 J K⁻¹ mole⁻¹ smaller than the observed ones. The difference between the experimental and the calculated values is roughly explained by taking into account the cation-exchange reaction between the tetrahedral and the octahedral sites in the spinel structure.

Observation of a Phase Transition in ThBr₄ and ThCl₄ Single Crystal by Far Infrared and Raman Spectroscopy Study. S. HUBERT*, P. DELAMOYE, S. LEFRANT, M. LEPOSTOLLEC, AND M. HUSSON-NOIS, Laboratoire de Radiochimie, Institut de Physique Nucléaire, B.P. 1, 91406 Orsay, France. At 4 K the visible and infrared absorption and emission spectra of U^{4+} in $ThBr_4$ and $ThCl_4$ single crystals are not very consistent with what is predicted by the selection rules for the room-temperature structure. Thus we investigated Raman scattering in the temperature range 10 – 300 K to look for a structure change and obtain a better understanding of the spectroscopy of U^{4+} in $ThBr_4$ and $ThCl_4.$ At room temperature, the observed Raman lines have been assigned on the basis of a D_{4h} factor group analysis. The study of the temperature dependence of the Raman spectra permitted us to discover phase transitions of $ThBr_4$ and $ThCl_4$ at 95 and 70 K, respectively. The splitting observed for the strongest E_g symmetry mode shows a lowering of the symmetry below the transition point. Powder X-ray diffraction at 77 K of hygroscopic $ThBr_4$ is being carried out to determine the low-temperature structure.

Chemical Diffusion in Intermediate Phases in the Lithium–Tin System. C. JOHN WEN AND ROBERT A. HUGGINS*, Department of Materials Science and Engineering, Stanford University, Stanford, California 94305. The compositional variation of the chemical diffusion coefficient in the six intermediate phases $LiSn, Li_2Sn_3, Li_5Sn_2, Li_{13}Sn_5, Li_7Sn_2,$ and $Li_{22}Sn_5$ of the lithium–tin system at $415^\circ C$ has been measured. Among these intermediate phases, the phase $Li_{13}Sn_5$ has the highest chemical diffusion coefficient, varying with composition from 5.01×10^{-5} to 7.59×10^{-4} cm²/sec at that temperature. Combining this information with coulometric titration curves (EMF versus composition), the self-diffusion coefficient of lithium has also been determined in the various intermetallic phases as a function of composition under the assumption that the tin atoms do not move appreciably compared with the lithium atoms. The lithium self-diffusion coefficient in the phase $LiSn$ is lower than those in the more lithium-rich phases by one order of magnitude. This result is discussed in terms of the difference between the crystal structures of $LiSn$ and the other lithium-rich phases in the lithium–tin system.

Bulk Magnetic and Neutron Diffraction Data for the Pyrochlore Yb₂V₂O₇: Evidence for Ferromagnetic Coupling between Yb³⁺ and V⁴⁺ Moments. LYNNE SODERHOLM, J. E. GREEDAN*, AND M. F. COLLINS, Institute for Materials Research McMaster University, Hamilton, Ontario L8S 4M1, Canada. Bulk magnetic data for the pyrochlore material $Yb_2V_2O_7$ have been redetermined and compared with existing literature values. Susceptibility data from 300 to 77 K can be interpreted in terms of Curie–Weiss behavior above about 170 K, yielding the parameters $C_m = 6.0$ cm³ mole⁻¹ K⁻¹ and $\theta_c = -20$ K. This θ_c is slightly more negative than values reported previously. The saturation moment at 4.2 K is $5.3 \pm 1 \mu_B,$ significantly greater than that reported previously. The magnetization versus temperature curve shows evidence for the ferromagnetic ordering of the V^{4+} sublattice at 73 K and the ferromagnetic ordering of the Yb^{3+} sublattice at about 30 K. The shape of the magnetization–temperature curve is most easily interpreted in terms of ferromagnetic coupling between the V^{4+} and Yb^{3+} sublattices. Neutron diffraction data at 7 and 100 K confirm the ferromagnetic model and yield a value of $1.7 \pm 2 \mu_B$ for the Yb^{3+} moment. This reduced moment (free ion = $4.0 \mu_B$) is consistent with crystal-field parameters found for the isostructural $Yb_2Ti_2O_7$ which has a similar lattice constant.