

## Abstracts of Forthcoming Articles

*Partial Decomposition of Dolomite in CO<sub>2</sub>.* H. HASHIMOTO, E. KOMAKI, F. HAYASHI, AND T. UEMATSU, Faculty of Engineering, Chiba University, Yayoicho, Chiba-shi, Japan. Thermal decomposition of dolomite into CaCO<sub>3</sub> and MgO under CO<sub>2</sub> was investigated by isothermal kinetic measurements, X-ray diffraction analysis, and electron diffraction. The decomposition was described as an interfacial reaction. Crystalline CaCO<sub>3</sub> is formed in an extremely oriented state even if the temperature is higher than the decomposition temperature of calcite, at least at the earlier stage of the decomposition. The crystallites of MgO grow with time and temperature, while the grain size of CaCO<sub>3</sub> remains constant during the isothermal decomposition. The CaCO<sub>3</sub> crystallite size is a minimum at about 750°C. The classical theories of the mechanism of formation of CaCO<sub>3</sub> from dolomite were reexamined, and a direct formation theory was suggested on the basis of the results of X-ray analysis.

*Solid-State Reaction between Thallous Carbonate and 8-Hydroxyquinoline.* N. B. SINGH, R. P. SINGH, J. SINGH, AND H. C. SINGH, Department of Chemistry, University of Gorakhpur, Gorakhpur (U.P.), India. The solid-state reaction between thallous carbonate and 8-hydroxyquinoline has been studied. The energy of activation for surface migration was found to be 8.8 kcal/mole whereas for inner penetration it was 14.6 kcal/mole. The reaction product was characterized by elemental analysis and ir spectral studies.

*Resonance Paramagnetique Electronique du Centre F<sup>+</sup> dans les Fluorapatites Carbonatees de Type B.* GERARD BACQUET, VO QUANG TRUONG, GILBERT BONEL, AND MIREILLE VIGNOLES, Laboratoire de Physique des Solides, CNRS, Université Paul Sabatier, 31077 Toulouse Cédex, France. Samples of B-type carbonated fluorapatites were heated at 450°C, X-irradiated at room temperature, and then annealed at 150°C. The ESR spectrum obtained after such a treatment was attributed to an electron trapped at an oxygen vacancy (F<sup>+</sup> center). The intensity of this spectrum increases with the amount of carbonate ions present in the specimens, then decreases. Such behavior was correlated with the number of oxygen vacancies present in the samples as a function of the carbonate content. Our results support the structural model proposed for these compounds.

*P-T-X Phase Equilibrium Study of New Solid Solution Systems, Cd<sub>1-x</sub>M<sub>x</sub>S (M = Mg, Ca, Sr).* TOSHIO KOBAYASHI, KENZO SUSA, AND SATOSHI TANIGUCHI, Central Research Laboratory, Hitachi Ltd., Tokyo 185, Japan. Pressure, temperature, and composition phase equilibrium diagrams of new solid solution systems of the Cd<sub>1-x</sub>M<sub>x</sub>S (M = Mg, Ca, Sr) type were investigated using the quenching method. The stable region for the rock salt-type phase is widely extended toward the high temperature-low pressure region by substituting 10-20 mole% of Cd with Ca or Sr. Temperature and composition phase diagrams for each solid solution system were obtained at 2 GPa. The rock salt-type phase stability is discussed in view of these phase relations.

*Etude Cristallographique Comparee et Conductivite Electrique de Deux Tellurates Mixtes: Ag<sub>x</sub>Na<sub>2-x</sub>Te<sub>2</sub><sup>IV</sup>Te<sub>3</sub><sup>VI</sup>O<sub>14</sub> (x = 0, 4) et K<sub>2</sub>Te<sup>IV</sup>Te<sub>3</sub><sup>IV</sup>O<sub>12</sub>.* WALOEJO LOEKSMANTO, JACQUES MORET, MAURICE MAURIN, AND ETIENNE PHILIPPOT, Laboratoire de Chimie Minérale C, Université des Sciences et Techniques du Languedoc, Place Eugene Bataillon, 34060 Montpellier Cedex, France. Ag<sub>x</sub>Na<sub>2-x</sub>Te<sub>2</sub><sup>IV</sup>Te<sub>3</sub><sup>VI</sup>O<sub>14</sub> (x = 0.40) is monoclinic, space group P2<sub>1</sub>/c with a = 6.332(2), b = 24.681(8), c = 7.308(2) Å, β = 110.84°, and Z = 4. The structure refinement was performed to a final R value of 0.041. The tridimensional network is characterized by corner-sharing octahedral sheets (Te<sup>VI</sup>O<sub>4</sub>)<sub>n</sub>, with hexagonal sites as in the K<sub>2</sub>Te<sup>IV</sup>Te<sub>3</sub><sup>VI</sup>O<sub>12</sub> and Te<sub>2</sub><sup>IV</sup>O<sub>8</sub> groups. The differences between these two crystal structures are discussed in terms of ionic radii of Na, Ag, and K cations. The results of electric conductivity measurements on homogenous ceramic disks are reported.

*Mössbauer <sup>57</sup>Fe Spectra Exhibiting "Ferrous Character."* G. A. FATSEAS AND JOHN B. GOODENOUGH, Laboratoire de Chimie des Solides, CNRS, 2 rue de la Houssinière, 44072 Nantes Cedex, France. The term "ferrous character" reported extensively in the literature for the Mössbauer spectroscopy of octahedrally coordinated iron atoms in chalcogenides and antimonides is critically evaluated. The significance of a formal valence state for the iron is examined. The magnitude of the isomer shift is shown to provide a guide not only to the existence of high-spin versus low-spin states, but also to

localized versus itinerant electrons or to extended electrons within Fe- $X$ - $M$  interactions ( $M$  = transition metal and  $X$  = anion). The existence of a quadrupole splitting for iron atoms in intrinsically cubic fields is only possible where the  $\beta$ -spin electron outside a closed  $\alpha$ -spin half-shell is localized and Jahn-Teller coupled to lattice vibrations to form vibronic states. This situation is distinguished from quadrupolar fields associated with local-site symmetries formed from cubic symmetry as well as from the case where the formation of itinerant  $\beta$ -spin electrons inhibits the formation of vibronic states.

*Etude de la Conductivite Ionique des Hydrurofluorures  $\text{CaF}_{2-x}\text{H}_x$ .* REMI LEVEQUE, MICHEL ZANNE, DENISE VERGNAT-GRANDJEAN, AND JEAN-FRANCOIS BRICE, Laboratoire de Chimie du Solide Minéral, Université de Nancy I, 54037 Nancy Cedex, France. The present work is concerned with the electrical conductivity of the calcium hydride fluorides  $\text{CaF}_{2-x}\text{H}_x$  between 20 and 200°C. The study was made using the complementary methods of complex admittance conductivity measurements and dielectric loss measurements. The influence of quenching and doping by  $\text{Na}^+$  has permitted us to identify the two conductivity domains observed. The low-temperature domain, which is characterized by a slight thermal increase in conductivity, corresponds to the reorientation of  $[\text{V}_{(\text{F,H})}^*-\text{Na}'_{\text{Ca}}]^*$  dipoles due to impurities. The second domain corresponds to the first stage of ionic conduction which results from the migration of  $\text{V}_{(\text{F,H})}^*$  vacancies formed by the thermal dissociation of  $[\text{V}_{(\text{F,H})}^*-\text{Na}'_{\text{Ca}}]^*$  complexes. The  $\text{H}^-/\text{F}^-$  substitution increases the mobility of charge carriers and the conductivity increases by the factor  $10^3$  between the compositions  $\text{CaF}_2$  and  $\text{CaFH}$ . Thus calcium hydride fluorides can be considered to be electrolytic solids with medium conductivity ( $\text{CaF}_{1.06}\text{H}_{0.94}$ :  $\sigma = 10^{-6} \Omega^{-1} \text{cm}^{-1}$  at 130°C).

*A Kinetic Study of Oxidation of Praseodymium Oxides:  $\text{PrO}_{1.714} + 0.032 \text{O}_2 \rightarrow \text{PrO}_{1.778}$ .* H. INABA, S. P. PACK, S. H. LIN, AND L. EYRING, Department of Chemistry, Arizona State University, Tempe, Arizona 85281. Kinetic and thermodynamic studies between the iota ( $n = 7$ ) and the zeta ( $n = 9$ ) phases of the homologous series of the praseodymium oxides ( $\text{Pr}_n\text{O}_{2n-2}$ ) have been carried out as a function of oxygen pressure at 535, 540, 550, and 570°C. The thermodynamic study was carried out by measuring the weight of the oxide sample at equilibrium at these temperatures as a function of pressure. The existence of a reproducible hysteresis loop which depends on the temperature and pressure is shown. The kinetic study was carried out by measuring the weight change of the sample as a function of time after a sudden increase of oxygen pressure initiated the reaction. In order to interpret the kinetic data, various theoretical models assumed, for example, to depend upon diffusion, a moving-boundary, a phase-boundary reaction-control, or nucleation and growth have been examined. None of these models, however, is capable of correlating the experimental data. It was found that for the powder sample diffusion of oxygen is much faster than the rate of reaction and the reaction kinetics is first order with respect to both the concentration of reactant and the ambient oxygen pressure. A linear plot of the reaction rate versus the ambient pressure extrapolates to a finite pressure at zero rate, suggesting that the reaction does not begin until this pressure is attained. It has been shown that this pressure corresponds to the minimum required to produce zeta phase as shown by the isothermal hysteresis loop along the oxidation path. From the measurements of the oxygen pressure and the temperature dependence of the observed rate constants, the activation energy of the reaction was determined to be 45.3 kcal/mole.

*Tetragonal-to-Cubic Transformation of Hausmannite.* EMIL POLLERT, Institute of Physics, Czechoslovak Academy of Science, Na Slovance 2, 180 40 Praha 8, Czechoslovakia. The tetragonal-to-cubic transformation of hausmannite,  $\text{Mn}_3\text{O}_4$ , was studied by X-ray, high-temperature analysis. The transformation exhibits properties characteristic for diffusionless processes, i.e., the coexistence of regions of the tetragonal and cubic phases, and hysteresis. The position of the coexistence region with regard to the temperature depends on the oxygen stoichiometry and/or concentration of  $\text{Mn}^{3+}$  ions.

*Magnetism and Phase Relations of the  $\text{PrAl}_2$ - $\text{CaAl}_2$ ,  $\text{GdAl}_2$ - $\text{CaAl}_2$  Systems.* TOMAS RIVILLO AND W. E. WALLACE, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania. The magnetic properties and phase relations of the ternary systems  $\text{Pr}_{1-x}\text{Ca}_x\text{Al}_2$  and  $\text{Gd}_{1-x}\text{Ca}_x\text{Al}_2$  are reported. The first system exhibits complete miscibility whereas the second shows a miscibility gap extending from  $x = 0.5$  to 0.8. The ternaries were examined magnetically to ascertain whether anti-ferromagnetism could be produced by replacing the trivalent rare earth ion with divalent Ca. Results for the (Pr, Ca) $\text{Al}_2$  system give some indication that the exchange changes sign when 80% or more of the Pr is replaced by Ca. The  $\alpha$  phase (Gd-rich) alloys in the (Gd, Ca) $\text{Al}_2$  system are ferromagnetic with Curie temperatures only modestly reduced from that of  $\text{GdAl}_2$ . The  $\beta$  phase (Ca-rich) alloys in this system are