

radiolysis, and low-temperature (250–260°) thermal decomposition are identical; FeC_2O_4 is missing among the principal final solid state products. Arguments are presented in favor of the view that the Fe(II)-containing final product of photodecomposition is a polymer of composition $(\text{K}_2[\text{Fe}(\text{C}_2\text{O}_4)_2])_n$. On the basis of the experimental and literature data, the flow sheet and stoichiometry of the photodecomposition has been determined. A comparison is made of the spectral dependences of photoconductivity and of photolysis in air. The type of charge carrier is established. Questions related to the mechanisms of photodecomposition are discussed.

Structure de l'Oxyfluorure de Tantale et de Sodium $\text{Na}_2\text{Ta}_2\text{O}_5\text{F}_2$ β . M. VLASSE, J. P. CHAMINADE, J. C. MASSIES, AND M. POUCHARD. Service de Chimie Minérale Structurale de l'Université de Bordeaux I, associé au CNRS, 351 cours de la Libération, 33405 Talence, France. The crystal structure of sodium tantalum oxyfluoride, β - $\text{Na}_2\text{Ta}_2\text{O}_5\text{F}$ has been determined from single crystal diffraction data. The symmetry is monoclinic, space group $C2/m$ with a cell having dimensions: $a = 12.855 \pm 0.008$, $b = 7.349 \pm 0.005$, $c = 12.833 \pm 0.003 \text{ \AA}$, $\beta = 108.97 \pm 0.05^\circ$ and containing 8 formula units. The structure was refined by full-matrix least squares to a final R value of 0.072. The structure consists of 2 interpenetrating sublattices: the first, which has the overall formula $\text{Ta}_{16}\text{X}_{52}$, is made up of TaX_6 octahedra and the second with an overall formula Na_{14}X_4 is composed of Na_4X tetrahedra. The 2 remaining sodium atoms occupy the center of a hexagonal bipyramid. This arrangement can be described as a succession of weberite and pyrochlore type slabs parallel to the [001] direction.

Kinetics Studies of the Reactions of KMnO_4 and of KIO_4 in Alkali Halide Disks. H. S. KIMMEL, J. P. CUSUMANO AND D. G. LAMBERT. Department of Chemical Engineering and Chemistry, Newark College of Engineering, Newark, New Jersey 07102. The kinetics of the solid state reactions of KMnO_4 in alkali halide matrices and KIO_4 in alkali halide matrices were studied. All reactions were found to be first-order with respect to the species being reduced. Rate constants were determined at 25, 50, and 100 C, and activation energies were determined for the reactions of KMnO_4 in KI and KIO_4 in KI. At 25 C, the rate constants for the reaction of KMnO_4 in KI and KMnO_4 in RbI were approximately the same. But the rate constant at 25 C for the reaction of KIO_4 with I^- was about $2\frac{1}{2}$ times larger in a RbI disk than in a KI disk. Possible mechanisms for the solid state processes are suggested.

The Lanthanum Hydroxide Fluoride Carbonate System: The Preparation of Synthetic Bastnaesite. J. M. HASCHKE. Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104. Hydrothermal phase equilibria in the lanthanum + hydroxide + fluoride + carbonate system have been investigated along an isobaric and isothermal section of variable metal to fluoride ratio, x . Quantitative substitution of fluoride into LaOHCO_3 proceeds with the formation of a continuous solid solution, $\text{La}(\text{OH})_{1-x}\text{F}_x\text{CO}_3$, for $0 \leq x < 1$ and a two-phase region, $\text{LaFCO}_3 + \text{LaF}_3$, for $1 < x < 3$. Single crystal X-ray diffraction data show that untwinned LaOHCO_3 is an orthorhombic phase ($a = 21.891(5)$, $b = 12.639(3)$ and $c = 10.047(2) \text{ \AA}$) which is not isostructural with LaFCO_3 . Hydrolysis of the $\text{La}(\text{OH})_{1-x}\text{F}_x\text{CO}_3$ phase to the corresponding UCl_3 -type $\text{La}(\text{OH})_{3-x}\text{F}_x$ compositions has been observed. Thermal decomposition reactions of the hydroxide fluoride carbonates are described, and a geochemical process for the formation of bastnaesite and tysonite is proposed.

Stability of Two Cobalt Titanate Defect Spinels. J. P. SHARPLES AND A. NAVROTSKY. Department of Chemistry, Arizona State University, Tempe, Arizona 85281. Preparation of the defect spinels $\text{Ti}_3\text{Co}_2\text{O}_8$ and $\text{Ti}_4\text{Co}_4\text{O}_{12}$ was attempted by solid state exchange reactions. $\text{Ti}_4\text{Co}_4\text{O}_{12}$ was successfully synthesized but attempts at preparing pure $\text{Ti}_3\text{Co}_2\text{O}_8$ were unsuccessful. The enthalpy of transformation of $\frac{1}{4} \text{Ti}_4\text{Co}_4\text{O}_{12}$ to CoTiO_3 (ilmenite) was determined by calorimetry, $\Delta H_{298}^\circ = -1.7 \pm 1.0 \text{ kcal/mole}$.

Etude Cristallographique et Magnétique de la Solution Solide $\text{Fe}_{2-2x}\text{Ni}_{1+x}\text{Sn}_x\text{O}_4$. C. DJEGA-MARIADASSOU, F. BASILE, AND P. POIX. E. R. 83 du C.N.R.S. Université de Paris XI, Laboratoire de Chimie minérale, Batiment 420, Centre Scientifique d'Orsay, 91405 Orsay, France. Crystallographic and magnetic measurements made on $\text{Fe}_{1-x}\text{Ni}_{1-x}\text{Sn}_x\text{O}_4$ ferrites indicate a large proportion of the Fe^{3+} ions are on A sites but do not specify what are the respective amounts of Ni^{2+} and Sn^{4+} on the A sites. Ni^{2+} concentration on B sites cannot be greater than 1.26 and thus the rate of substitution is limited by $x = 0.37$. As shown by the values of α and β determined from magnetic measurements, the magnetization

curves transform from Q type for Fe_2NiO_4 to P type for $x \geq 0.1$. The nature of interactions between magnetic ions has been deduced from sign and values of n , α , β .

Etude Magnetique de Compose $\text{SrTb}_2\text{Fe}_2\text{O}_7$. Determination des Structures Magnetiques par Diffraction Neutronique. D. SAMARAS, A. COLLOMB, J. C. JOUBERT AND E. F. BERTAUT. Laboratoire des Rayons X, C.N.R.S., B. P. No. 166, Centre de Tri, 38042 Grenoble Cedex, France. Magnetic properties of the compound $\text{SrTb}_2\text{Fe}_2\text{O}_7$ (space group $P4_2/mnm$) have been investigated by magnetic measurements of susceptibility and magnetization and by neutron diffraction. The Néel temperature of the iron sublattice is 628°K. At 295°K the configuration of the Fe^{3+} spins is $G_x^- \pm A_y^-$ (antiferromagnetic). At 4.2°K the configuration of Tb^{3+} spins is represented by the modes F_x^+ , C_y^- , A_z^- coupled in the representation E_g with the mode A_z^- of the Fe^{3+} spins. The values of the magnetic moments corresponding to the different modes are obtained from the magnetic structure refinement. The value of the F_x^+ ferromagnetic mode of Tb^{3+} is $2.6 \mu_B/\text{ion}$ at 4.2°K. At room temperature the orientation of Fe^{3+} spins perpendicularly to the c axis seems to be due to a site anisotropy, the easy direction coinciding with the axis of the FeO_5 bipyramids. The reorientation of Fe^{3+} spins along the c axis observed at 4.2°K can be explained by a strong Fe^{3+} - Tb^{3+} coupling which overcomes the Fe^{3+} one ion anisotropy. The low site symmetry (m) of Tb lifts the degeneracy completely and gives rise to a pseudodoublet (formed by two singlets of small separation) associated with an Ising-like behavior. In fact the Tb^{3+} spins are in the m planes, containing the c -axis.

Etude de Nouveaux Oxydes Ternaires d'Europium Divalent, de Type Bronze Oxygene de Tungstene Quadratique et de Type Peroxskite. J. P. FAYOLLE, F. STUDER, G. DESGARDIN, AND B. RAVEAU. Groupe de Cristallographie et Chimie du Solide, ERA 305, Laboratoire de Chimie Minérale du Solide, Université de Caen, 14032 Caen, France. New divalent europium ternary oxides have been isolated and studied by X-ray diffraction and electron microscopy. Fifteen of them crystallize with tetragonal bronzelike structures: EuM_2O_6 ; $\text{Eu}_6\text{M}_{34}\text{O}_{64}$ ($M = \text{Ta}, \text{Nb}$); $\text{EuBCM}_5\text{O}_{15}$ ($B = \text{Ca}, \text{Eu}, \text{Ba}$; $C = \text{Na}, \text{K}$; $M = \text{Ta}, \text{Nb}$) and $\text{Eu}_{0.60}\text{NbO}_3$. The compound Eu_xNbO_3 ($0.80 \leq x \leq 0.90$) is of perovskite type. Structural evolution of these phases, compared to the strontium homologous compounds, is discussed.

Etude Structurale des Systemes Ln_2S_3 - GeS_2 . A. MICHELET, A. MAZURIER, G. COLLIN, P. LARUELLE, AND J. FLAHAUT. Laboratoire de Chimie Structurale, C.N.R.S. No. 200, Faculté des Sciences Pharmaceutiques et Biologiques, 4, Avenue de l'Observatoire, Paris 6, France. In the systems formed between the Ln_2S_3 sulfides of the rare earth and GeS_2 , three kinds of new crystal structures are observed: $\text{Ln}_4\text{Ge}_3\text{S}_{12}$, rhombohedral $R3c$; Ln_2GeS_5 monoclinic $P2_1/a$; $\text{Ln}_6\text{Ge}_2\text{S}_{14}$, hexagonal superstructure $P6_3$ of the $\text{Ce}_6\text{Al}_{10/3}\text{S}_{14}$ structure. The three structures are established from single crystals studies. Germanium atoms are inside isolated tetrahedra of sulfur atoms. Lanthanide atoms are inside two or three-capped trigonal prisms, often with very long equatorial Ln-S distances. The La_2GeS_5 compound belongs to the series of two anions compounds, with layers of [LaS] composition alternating with GeS_4 tetrahedra.

Influence de la Substitution de fer sur les Propriétés Magnetiques des Solutions Solides $\text{Ca}_2\text{Fe}_{2-x}\text{M}_x\text{O}_5$ ($M = \text{Al}, \text{Sc}, \text{Cr}, \text{Co}, \text{Ga}$). J. C. GRENIER, M. POUCHARD, AND P. HAGENMULLER. As dicalcium ferrite the derived phases of formula $\text{Ca}_2\text{Fe}_{2-x}\text{M}_x\text{O}_5$ ($M = \text{Al}, \text{Sc}, \text{Cr}, \text{Co}, \text{Ga}$) contain two different sites for the trivalent cations. The cationic distribution between the sites is obtained by Mössbauer spectroscopy. The evolution of the ordering temperature can be explained by this distribution; the thermal variation of the magnetic susceptibilities allows an estimation of the relative values of the couplings.

Magnetic Ordering in $\text{Ba}_2\text{MnReO}_6$. C. P. KHATTAK, D. E. COX AND F. F. Y. WANG. Department of Materials Science, SUNY at Stony Brook, New York 11790. The ordered perovskite $\text{Ba}_2\text{MnReO}_6$ has been reported to be ferrimagnetic with a Curie temperature of 105°K and a saturation moment of $3.9 \mu_B$, consistent with antiparallel coupling of spin-only moments of the combination Mn^{2+} - Re^{6+} . Neutron diffraction studies on polycrystalline material have confirmed that the Mn and Re ions are completely ordered chemically. At 4.6°K, two sets of magnetic peaks were observed, the stronger consistent with the ferrimagnetic model, and the weaker characteristic of antiferromagnetic ordering of the first kind, indicative of some canting of the moments in adjacent (001) planes. The moment on the Mn ion was found to be $4.8 \mu_B$, but that on the Re ion was found to be less than $0.2 \mu_B$ if a localized