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# Abstracts of Forthcoming Articles

*The Anderson–Grüneisen Parameter for Cubic Crystals.* S. R. Tripathi, D. C. Gupta, and M. N. Sharma. Department of Physics, Lucknow University, Lucknow-226007, India. A new, simple relation for $\delta$ the Anderson–Grüneisen parameter, developed by Sharma and Tripathi, which involves fewer approximations than other complex, cumbersome equations available in literature, has been used to compute values of $\delta$ employing three different potentials viz the Varshni–Shukla, the Logarithmic, and the Rydberg's function. The comparison of these values with experimental ones indicates the suitability of Varshni–Shukla and Logarithmic potential functions for the study of the property $\delta$.

*The effect of Crystal Size on the Thermal Explosion of α-Lead Azide.* M. M. Chaudri and J. E. Field. Physics and Chemistry of Solids, Cavendish Laboratory, Free School Lane, Cambridge, England. It is shown experimentally that the critical explosion temperature of α-lead azide single crystals in air decreases with increase in size of the crystals. The mode of decomposition of the crystals was examined with optical and scanning electron microscopy, and it was found that surface decomposition took place preferentially at localized regions; crystal break-up also occurred. Calculations of explosion temperature for the case of parallelopiped shaped particles in air were made. The predicted decrease in the explosion temperature for an increase in crystal thickness from 4 to 34 μm (minimum dimension) was 6°K, whereas the experimental value was ~30°K. It is suggested that the difference between the experimental and theoretical results is due to the mode of decomposition during the preexplosion period. For crystals of thickness less than ~3 μm neither explosion or melting took place even for temperatures as high as 825°K.

*Preparation and Properties of $LnMX_3$ Where Ln = Rare Earths, Bi; M = Ta, Nb, Ti, V and X = S, Se.* P. C. Donohue. Central Research Department, E. I. du Pont de Nemours and Co., Experimental Station, Wilmington, Delaware 19898. Compounds were prepared of the general formula $LnMX_3$ (where Ln = all rare earths or Bi, X = S, and M = Ta or Nb; Ln = La through Tb, X = S, and M = Ti or V; Ln = La through Gd, X = Se, and M = Ta or Nb; Ln = La, X = Se, and M = Ti or V). They were prepared by reaction of the elements in evacuated silica tubes with iodine as a mineralizing agent. They form as black shiny lamella crystals which exhibit plastic deformation, good thermal and hydrolytic stability, low coefficients of friction, and metallic conductivity. The crystal structures have subcells like $PbNbS_3$ but the actual cells are larger and more complex. The series is isotypic with $LaCrS_3$.

*Defect Ferroelectrics of Type $Pb_{1-x}TiO_{3-x}$.* S. Shirasaki, K. Takahashi, H. Yamamura, K. Kakegawa, and J. Mori. National Institute for Researches in Inorganic Materials, Sakura-Mura, Niihari-Gun, Ibaraki, Japan. A series of new ferroelectric substances of type $Pb_{1-x}TiO_{3-x}$ or $Pb_{1-x}Na_yTiO_{3-x+(y/2)}$ with perovskite-type structure was prepared by simple solid state reaction among powdered mixtures of PbO, $TiO_2$, and in several cases, $Na_2CO_3$, with $TiO_2$ in an excess. The defect materials are characterized in terms of inhomogeneously distributed vacancies, $\square_{Pb}$ and $\square_{O}$ at the respective equivalent lattice positions. Their ferroelectric properties are discussed in relation to those of the same type of materials precipitated aqueously and followed by firing at elevated temperatures.

*The Photochemistry of Potassium Trisoxalatoferrate(III) Trihydrate in the Solid State.* G. G. Savelyev, A. A. Medvinskii, V. L. Shtsherinskii, L. P. Gevlitch, N. I. Gavryusheva, Yu. T. Pavlyukhin, and L. I. Stepanova. Department of General and Inorganic Chemistry, Polytechnic Institute, Tomsk, USSR. The gaseous and solid state products of decomposition on uv exposure of polycrystalline $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ have been investigated by mass spectroscopy, ir- and Mössbauer spectroscopy, and chemical and X-ray phase analysis. $CO_2$ and CO are obtained as photoproducts. The volume ratio, $CO:CO_2$, generated depends on the exposure conditions and approximately equals 1:3 on photodecomposition in air and 1:2 on decomposition in vacuum. Comparison of the experimental and literature data leads to the following conclusions: the Fe(II)-containing final products of photolysis, 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 $(K_2[Fe(C_2O_4)_2])_n$. 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* $Na_2Ta_2O_5F_2$ *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-$Na_2Ta_2O_5F$ has been determined from single crystal diffraction data. The symmetry is monoclinic, space group $C2/m$ with a cell having dimensions: $a = 12.855 \pm 0.008$, $b = 7.349 \pm 0.005$, $c = 12.833 \pm 0.003$ Å, $\beta = 108.97 \pm 0.05°$ 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 $Ta_{16}X_{52}$, 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, $La(OH)_{1-x}F_xCO_3$, for $o \leqslant x < 1$ and a two-phase region, $LaFCO_3 + LaF_3$, 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 $c = 10.047(2)$ Å) which is not isostructural with $LaFCO_3$. Hydrolysis of the $La(OH)_{1-x}F_xCO_3$ phase to the corresponding $UCl_3$-type $La(OH)_{3-x}F_x$ 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 $Ti_3\square Co_2O_8$ and $Ti_4\square Co_4O_{12}$ was attempted by solid state exchange reactions. $Ti_4\square Co_4O_{12}$ was successfully synthesized but attempts at preparing pure $Ti_3\square Co_2O_8$ were unsuccessful. The enthalpy of transformation of $\frac{1}{4}$ $Ti_4\square Co_4O_{12}$ to $CoTiO_3$ (ilmenite) was determined by calorimetry, $\Delta H^\circ_{298} = -1.7 \pm 1.0$ kcal/mole.

*Etude Cristallographique et Magnetique de la Solution Solide* $Fe_{2-2x}Ni_{1+x}Sn_xO_4$. 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 $Fe_{1-x}Ni_{1-x}Sn_xO_4$ 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 $\alpha$ and $\beta$ determined from magnetic measurements, the magnetization