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# Abstracts of Forthcoming Articles

*Preparation of the $HgCr_2(Se_xS_{1-x})_4$ Type Compounds and the X-Ray Control of the Process of Formation of their Spinel Structures.* I. OKONSKA-KOZLOWSKA, D. KONOPKA, M. JELONEK, J. HEIMANN, J. PIETKIEWICZ, AND A. CHELKOWSKI. Uniwersytet Slaski, Instytut Fizyki, ul. Uniwersytecka 4, 40–007 Katowice, Poland. Compounds of the $HgCr_2(Se_xS_{1-x})_4$ type were prepared for $0.750 \leqslant x \leqslant 0.250$ by the thermal synthesis from parent elements. Individual reaction stages were controlled röntgenographically. The values of electric conductivity activation energy of the compounds have been calculated and the chemical analysis of the substances prepared has been developed.

*Apatites of Divalent Europium.* I. MAYER, E. FISCHBEIN, AND S. COHEN. Department of Inorganic and Analytical Chemistry, Hebrew University of Jerusalem, Israel. The preparation methods of $Eu_3(PO_4)_2$, $Eu_5(PO_4)_3F$, $Eu_3(PO_4)Cl$, and $Eu_5(AsO_4)_3OH$ are described. $Eu_3(PO_4)_2$ crystallizes in a rhombohedral unit cell and the apatite like compounds in the $P6_3/m$ hexagonal structure. All the compounds are isomorphous with the corresponding Sr compounds, and similar in size. Magnetic susceptibility measurements show that $Eu_3(PO_4)_2$ is magnetically ordered below 5°K and $Eu_5(PO_4)_3F$ and $Eu_5(PO_4)_3Cl$ are paramagnetic. Solid solution of the $Eu_{5-x}Ca_x(PO_4)_3F$ system obey Vegard's law, while the $Eu_{5-x}Ba_x(PO_4)_3F$ and $Eu_{5-x}Ba_x(PO_4)_3Cl$ systems show a trend to form ordered solid solutions.

*Phase Equilibria, Thermal Analysis, and Reactivity of Tin Tungsten Bronzes and Related Phases.* I. J. MCCOLM, R. STEADMAN, AND C. DIMBYLOW. School of Materials Science, University of Bradford, Bradford BD7 1DP, England. Crystal chemistry and phase relations of the bronze forming region of the Sn–W–O system have been investigated. Above 780°C the tin bronzes $Sn_xWO_3$ are shown to be thermally unstable and an equilibrium diagram is established at 700°C which shows that the composition limits of the tetragonal phase are $0.21 \leqslant x \leqslant 0.29$. Below $x = 0.21$ a series of single and two-phase regions containing orthorhombic bronzes exists for which the composition limits have been established. In the range $0.29 \leqslant x \leqslant 0.76$ the system comprises the tetragonal bronze, $Sn_2W_3O_8$ and $SnWO_4$, while above 0.76 there is no bronze, only $Sn_2W_3O_8$, $SnWO_4$ and free Sn. The phase $Sn_2W_3O_8$ has been isolated and shown to have a hexagonal unit cell, $a = 7.696$ Å, $c = 18.654$ Å. The evidence of differential thermogravimetric analysis (DTA) and X-ray studies suggests that this hexagonal phase arises from the decomposition of the tungsten bronze phase and is itself decomposed to cubic $SnWO_4$ above 700°C. Small thermal effects observed in the DTA scans of tin-containing tetragonal bronzes are interpreted in terms of an order–disorder phenomenon arising from asymmetric tunnel occupancy by $Sn^{2+}$ ions caused by the presence of the lone pair of electrons. Hydrogen reduction of $Sn_xWO_3$ has been shown to result in complete removal of oxygen, producing $Sn + \alpha$-W in the range 600–850°C. Some activation energy data are given for the reduction process.

*Structural Relationships, Crystal Chemistry and Anion Substitution Processes for $M(III)X_3$ Systems of the Lanthanides and Actinides.* J. M. HASCHKE. Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104. An examination of data for lanthanide and actinide phases with $UCl_3$-type and $PuBr_3$-type $M(III)X_3$ structures has shown that these systems are conveniently described by alternating layers of $[MX_2]_n^{n+}$ and $[X]_n^{n-}$. The relationships between the $UCl_3$- and $PuBr_3$-type structures are described and expanded to include a variety of anion substitution systems, $M(III)X_{3-x}Y_x$. The two different types of $[MX_2]_n^{n+}$ layers observed in these systems are consistent with the existence of a novel structural unit, $[M_2X_4]^{2+}$. The effects of radius ratio constraints and layering mechanisms on the phase equilibria and anionic substitution processes, polymorphism and crystal growth in the $MX_{3-x}Y_x$ systems are discussed.

*Chemical Self-Diffusion in CdTe.* S. S. CHERN AND F. A. KRÖGER. Department of Materials Science, University of Southern California, Los Angeles, California 90007. The diffusion constant determining the rate of variation in the stoichiometric composition of CdTe for a change in cadmium pressure is

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measured for indium-doped crystals. The results for doped as well as undoped crystals are expressed in terms of previously determined equiconcentration tracer diffusion constants using a detailed point defect model. Factors responsible for asymmetrical behavior are discussed.

*$Hg_2M_2F_6S$ et $Hg_2M_2F_6O$: Deux Nouvelles Familles de Pyrochlores Contenant du Mercure et des Metaux M de Transition Divalents.* D. Bernard, J. Pannetier, and J. Lucas. Université de Rennes, U.E.R. Laboratoire de Chimie Minérale D, Avenue du General Leclerc, 35031 Rennes Cedex, France. New pyrochlore compounds $Hg_2M_2F_6S$ (M = Zn, Cu, Ni, Co, Mn, Mg) and $Hg_2M_2F_6O$ (M = Zn, Cu, Ni, Co, Mg) have been prepared and characterized. They all have a cubic structure ($Fd3m$) except $Hg_2Cu_2F_6O$ which shows a tetragonal distortion. Refinement of crystal structures of five compounds from powder diffractometer intensities leads to a positional parameter $x(48f)$ lying from 0.315 to 0.319. The evolution of interatomic distances and independence of two networks $(Hg_2X')^{2+}$ and $(M_2F_6)^{2-}$ are examined.

*Luminescence and Vibrational Spectra of $Ba_5Li_2W_3O_{15}$.* G. Blasse. Solid State Chemistry Department, Physical Laboratory, State University, Utrecht, The Netherlands. The infrared and raman spectra of $Ba_5Li_2W_3O_{15}$ are reported down to 200 $cm^{-1}$. From the internal stretching modes of the tungstate octahedra the crystallographic order between lithium and tungsten in the face-sharing octahedra can be derived. The green tungstate luminescence shows a low quenching temperature which is described with the Dexter–Klick–Russell model. The $U^{6+}$ ion shows a yellow emission in $Ba_5Li_2W_3O_{15}$. There is ample evidence for two different $U^{6+}$ centres with different decay times (10 and 80 $\mu$sec) and different emission and excitation spectra. One of these is located in a single layer of tungstate octahedra, the other in a double layer of octahedra.

*Hydrothermal Crystal Synthesis in the $Ho_2O_3(Yb_2O_3)$–$GeO_2$–$KF$–$H_2O$ Systems.* G. A. Emelchenko, L. N. Demyanets, A. N. Lobachev. Institute of Crystallography, Academy of Science, Moscow, U.S.S.R. Crystallization in the $Ho_2O_3(Yb_2O_3)$–$GeO_2$–KF–$H_2O$ systems has been investigated under hydrothermal conditions. Crystallization fields of the crystalline phases have been determined. Single crystals of $Ho_2Ge_2O_7$, $Yb_2Ge_2O_7$ (two types), $K_2HoF_5$, $K_2YbF_5$, $K_xYb_yGe_pO_q$ ($P$-type), $Ho(OH)_3$, $Yb(OH)_3$, and $K_2Ge_4O_9$ have been obtained. The germanates synthesized have been studied by X-ray analysis and ir-spectroscopy. Diorthogermanate $Yb_2Ge_2O_7$ has been found to crystallize in two structural types; the first is characterized by the usual structure that is typical for rare earth germanates, the second is new for germanates of rare earth elements. High chemical resistance is typical of these crystals. The $P$-type germanate also has a new type of structure among rare earth germanates. Some suggestions are made as to the structure of these new germanates on the basis of X-ray and ir-spectroscopic data.

*Low-Temperature Heat Capacity and Magnetic Studies on $DyCu_5$.* K. S. V. L. Narasimhan, M. J. Klein, and R. A. Butera. Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. Low temperature heat capacity studies on $DyCu_5$ revealed a $\lambda$-anomaly at 6.55 K. Evaluation of the entropy indicated that the ground state is not $(2J+1)$ fold degenerate. High field magnetization data yield a moment of 9.28 $\mu_B$ at 4.2 K and 120 kOe.

*Influence de la Substitution Tungstene–Niobium sur les Propriétés Cristallographiques et Dielectriques de la Solution Solide de Compositions Limites $Ba_{2,50-x}Na_{2x}Nb_5O_{15}$ $(0{,}23 \leqslant x \leqslant 0{,}60)$ le Systeme $BaNb_2O_6$–$(NaNbO_3)_2$–$(WO_3)_2$ a 1050°C.* J. M. Reau, B. Elouadi, J. Ravez, and P. Hagenmuller. Laboratorie de Chimie du Solide du C.N.R.S., Université de Bordeaux I, 351 Cours de la Liberation, 33405 Talence, France. The substitution of niobium by tungsten carried out in order to study its influence on the crystallographic and dielectric properties of the solid solution $Ba_{1.90}Na_{1.20}Nb_5O_{15}$–$Ba_{2.27}Na_{0.46}Nb_5O_{15}$ creates a large bidimensional homogeneity range of a tetragonal tungsten bronze type phase in the system $BaNb_2O_6$–$(NaNbO_3)_2$–$(WO_3)_2$. The presence of tungsten decreases the distorsion of the lattice as well as the ferroelectric Curie temperature. A transition from orthorhombic to tetragonal symmetry has been determined below Curie point.