Abstracts of Forthcoming Articles

The Crystal Structure of Tl-β-Alumina. T. KODAMA AND G. MUTO. The Institute of Industrial Science, The University of Tokyo, 22-1, Roppongi 7-chome, Minato-ku, Tokyo 106, Japan. The crystal structure of $Tl_2O \cdot 11Al_2O_3$ has been determined from three-dimensional X-ray data. The compound forms hexagonal crystals with $a = 5.598$, $c = 22.93$ Å and $z = 1$ in space group $P6_3/mmc$. The structure has been refined by least-squares methods with anisotropic temperature factors to an R value of 0.063 for 351 independent reflections collected by diffractometry. The crystal is composed of alternate stackings of the spinel block and the ion-conducting layer, both of which are linked together by the covalently bonded corner-sharing O_3Al–O–AlO_3 tetrahedra along the c-axis. The occupational percentages of the mobile ion were determined from the Fourier synthesis and compared with those of Ag- and Na-β-alumina.

A Single-Crystal Diffractometry Investigation of Iron in β-Rhombohedral Boron. B. CALLMER AND T. LUNDSTRÖM. Institute of Chemistry, University of Uppsala, Box 531, S75121 Uppsala, Sweden. The structure of a crystal of composition $FeB_{\sim 49}$ has been investigated using single-crystal diffractometry. The space group is $R\bar{3}m$ and the hexagonal cell dimensions are $a = 10.951$ Å and $c = 23.861$ Å. The three-dimensional boron network is essentially equivalent to that found in β-rhombohedral boron. Two sets of holes in this network are partially occupied by iron atoms.

The Ternary UO_2–UO_3–$EuO_{1.5}(EuO)$ System and Investigation of Eu(II)-Actinide(IV)-Perovskites. U. BERNDT, R. TANAMAS, AND C. KELLER. Institut für Radiochemie, Kernforschungszentrum, 75 Karlsruhe, Postfach 3640, Germany. At 1250°C, the following single-phase regions have been detected in the UO_2–UO_3–$EuO_{1.5}$ region of the ternary uranium–europium–oxygen system: (a) β-U_3O_8: no solubility for $EuO_{1.5}$ could be observed. (b) Fluorite phase: the oxygen limiting compositions are $(U, Eu)O_{2.25}$ and $(U, Eu)O_{1.79}$, respectively; the range of the stoichiometric composition MO_2 is between UO_2 and $(U_{0.36}, Eu_{0.64})O_2$, a fluorite phase with U(VI) is only obtainable for the substoichiometric region from $(U_{0.32}, Eu_{0.68})O_{1.98}$ to $(U_{0.24}, Eu_{0.76})O_{1.86}$. (c) Rhombohedral phase: It extends from $UO_3 \cdot 6EuO_{1.5}$ on the UO_3–$EuO_{1.5}$ side of the system to the $0.7UO_2 \cdot 0.3EuO_{1.5}$–$0.6UO_2 \cdot 0.4EuO_{1.5}$ line on the UO_2–$EuO_{1.5}$ side, showing an increased phase width with lowering of the uranium valency. (d) Monoclinic B-$EuO_{1.5}$: no solubility for UO_{2+x} could be observed. The first lanthanide–actinide perovskite compounds, orthorhombic $EuUO_3$ and $EuNpO_3$ could be prepared by different methods; attempts to prepare similar ternary oxides containing Th(IV), Pu(IV), and Am(IV), however, failed. EMF-measurements have proven that cubic C-$EuO_{1.5}$ is the thermodynamically stable $EuO_{1.5}$-modification below 1050 ± 20°C.

The Influence of Deviations from 1:1 Order in Perovskites on Optical Properties. K. C. BLEIJENBERG AND G. BLASSE. Physical Laboratory, State University, Sorbonnelaan 4, Utrecht, The Netherlands. Vibrational and electronic spectra of compositions $Ba_2Mg_{1-x}Li_{0.8x}W_{1+0.2x}O_6$ and $Sr_{1+x}La_{1-x}Li_{1-0.2x}W_{1+0.2x}O_6$ are reported. The vibrational spectra show the presence of clusters of WO_6^{6-} octahedra. Large clusters quench the luminescence that has been found for the compositions with $x = 0$.

Intermediate Phases and Pseudophases in the System WO_3–Nb_2O_5: Tetragonal Tungsten Bronze Phases. H. OBAYASHI AND J. S. ANDERSON. Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, England. Ordered intermediate phases with finely graded compositions are found in the Nb_2O_5–WO_3 system: homologous series of crystallographic shear phases for x in $MO_x(M = Nb + W) > 2.9$; a succession of block structures and intergrowth structures for $2.5 \leqslant x \leqslant 2.65$. The intermediate range has pentagonal tunnel structures partly based on the tetragonal tungsten bronze network. Ordered filling of some rational, but variable, fraction of tunnel sites could, in principle, generate a new closely graded series of phases. Synthetic experiments and lattice imaging electron

microscopy have been applied to this system. At least for the experimental conditions employed, the structure of the congruently melting $4Nb_2O_5 \cdot 9WO_3$, with 4/12 of pentagonal tunnels occupied, dominates the stability field. However, structures with 6/16 sites in a 2×2 TTB superlattice, and with 7/20 sites in a 5×1 TTB superlattice occupied form quite extended domains in a $4Nb_2O_5 \cdot 9WO_3$ matrix. In addition, the structure with 5/16 sites in a 2×2 TTB superlattice forms domains in preparations richer in WO_3 than $4Nb_2O_5 \cdot 9WO_3$, and this $2Nb_2O_5 \cdot 5WO_3$ structure itself shows evidence of ordered intergrowth with the $2Nb_2O_5 \cdot 7WO_3$ characterised electron microscopically by Iijima. The status of these ordered domain structures is discussed. Metastable structures may be effectively stabilised by coherent intergrowth with structures that are absolutely stable.

Nucleation Mechanism during Low Temperature Decomposition of Ammonium Perchlorate. E. F. KHAIRETDINOV, T. V. MULINA, AND V. V. BOLDYREV. Institute of Chemical Kinetics and Combustion, Siberian Branch of the Academy of Sciences of the U.S.S.R., Novosibirsk, 90. It is shown that proton-acceptor additions are effective inhibitors of the nucleation process of low-temperature decomposition of ammonium perchlorate (AP). In contrast to this, addition of ClO_3^- ion is a catalyst for the decomposition of AP: it increases the rate of nucleation V_n and the maximum concentration of nuclei N_{max} and decreases the induction period of nucleation τ. It is shown that addition of ClO_3^- ion is present in the purest commercial samples of AP. It is thought that the initiator of nucleation is $HClO_3$, i.e., $V_n = [H^+] \times [ClO_3^-]$. The dependence which is demonstrated agrees very well with experimental data on the influence of addition of proton donors and acceptors and also of additions of ClO_3^- ions on V_n. On the basis of this mechanism, means of regulating the temperature of initiation of AP decomposition are suggested. An explanation of the photosensitivity of AP exposed to the uv band is proposed.

On the Problem of Polymorphism and Fusion of Lanthanide Trifluorides. I. The Influence of Oxygen on Phase Transition Temperature. B. P. SOBOLEV, P. P. FEDOROV, AND D. B. SHTEYNBERG. Institute of Crystallography of the Academy of Sciences of the USSR, Lenisky pr. 59, Moscow B-117333, U.S.S.R. AND B. V. SINITSYN AND G. S. SHAKHKALAMIAN, State Institute of the Rare-Metal Industry, Moscow, U.S.S.R. The details of using thermal analysis (TA) in the investigation of lanthanide trifluorides are examined. By examining the literature on the problem of phase transitions in LnF_3 (Ln = lanthanum and the lanthanides) it is established that the basic reason for disagreement among the data of various authors is in most cases lack of control of pyrohydrolysis of LnF_3. For the first time the TA method is used to study parts of the state diagrams of the $LnF_3-Ln_2O_3$ systems (Ln = Gd, Tb, Ho, Er, and Y). Phases $LnF_{3-2x}O_x$ were $0 \leqslant x \leqslant 0.2$, which were not known earlier, are discovered. According to the type of interaction of LnF_3 with the corresponding Ln_2O_3, the trifluoride series is broken down into several groups corresponding to the structural type in which the LnF_3 crystallizes. The portions of the state diagrams of the $LnF_3-Ln_2O_3$ systems that were studied permit us to explain the reasons for contradictions in existing data on the temperatures of phase transformations in LnF_3.

On the Problem of Polymorphism and Fusion of Lanthanide Trifluorides. II. Interaction of LnF_3 with MF_2 (M = Ca, Sr, Ba), Change in Structural Type in the LnF_3 Series, and Thermal Characteristics. B. P. SOBOLEV, P. P. FEDOROV, AND N. L. TKACHENKO. Institute of Crystallography of the Academy of Sciences of the USSR, Lenisky pr. 59, Moscow B-117333, U.S.S.R. and K. B. SEIRANIAN, Erevan State University, Erevan, U.S.S.R. The results are presented of a study of the interaction of LnF_3 with MF_2 (M = Ca, Sr, Ba) for 34 binary systems of the LnF_3-MF_2 type in concentration range 60–100 mol% of LnF_3. It is shown that in this range the type of interaction of the components in the LnF_3-MF_2 systems is similar to that in the $LnF_3-Ln_2O_3$ systems. There is discussed the problem of stabilizing different structural types of LnF_3 (tysonite and α-YF_3) during the isomorphous replacement of Ln^{3+} by M^{2+} and $2F^{-1}$ by O^{2-} with formation of solid solutions $Ln_{1-x}M_xF_{3-x}$ and $LnF_{3-2x}O_x$, respectively. In the case of congruent fusion of these phases, the coordinates of the maximum on the fusibility curve (according to composition) are regularly displaced to the side of pure LnF_3 with a decrease in the atomic number of the lanthanide. The vacancy stabilized phases are typical examples of variable composition compounds (berthollides). On the basis of data on the interaction of components in the $LnF_3-Ln_2O_3$ and LnF_3-MF_2 systems, problems of polymorphism and changes of structural type in the LnF_3 series are discussed. Fusion and polymorphic transformation temperatures are given for LnF_3 with control of oxygen content in the specimens after thermal analysis.