Solubilité et Diffusion de l'Argent dans le Sulfure de Cadmium. A. GLEIZE AND F. CABANÉ-BROUTY. Laboratoire de Métallurgie, Université Aix-Marseille III, Faculté des Sciences et des Techniques, rue H. Poincaré, 13397, Marseille Cedex 4, France. Silver penetration is studied with a radiotracer technique. At 700°C, with an excess of cadmium, silver is principally incorporated as neutral interstitials and a very rapid diffusion is observed in single crystals. With an excess of sulfur, the dissolution as neutral interstitials cannot explain the measured solubilities. In pure single crystals, the penetration curves are complex and only a mean diffusion coefficient is obtained (at 700°C, $D = 2.10^{-8}\mathrm{cm}^2\mathrm{s}^{-1}$); in crystals presaturated with silver in the diffusion conditions, a diffusion along dislocations is superimposed to the point defect diffusion. The volume diffusion coefficients are found to be much smaller than those determined in pure crystals; the values obtained between 500 and 600°C led to an activation energy of 1.1 eV. In polycristalline samples the intergranular diffusion is important.

Phase Relations, Dopant Effects, Structure, and High Electrical Conductivity in the Na_2WO_4–Na_2MoO_4 Systems. P. H. BOTTELBERGHS AND F. R. VAN BUREN. Department of Inorganic Chemistry, Croesestraat 77A, Utrecht, The Netherlands. The x, T-phase diagram of the binary system Na_2WO_4–Na_2MoO_4 has been redetermined at ambient pressure, taking into account the influence of hysteresis effects. Thermodynamic calculations, based upon transition entropies as determined by precision DSC, indicate that the system is almost ideal with respect to the high-temperature phases. As anion dopes, Na_2SO_4 and Na_2CrO_4 give a metastable extension of the β-phase of Na_2WO_4 at decreasing temperature, involving some 40°C at 0.01 mole fraction of dopant. Cation dopes like Li_2WO_4 and K_2WO_4 behave quite differently. The electrical conductivity through the phase diagram is high in the α-phase ($\sigma \sim 10^{-2}\mathrm{mho.cm}^{-1}$) almost regardless of composition. The anomalous high conductivity of the β-phase decreases with increasing molybdate content. In pure Na_2MoO_4 an anomaly occurs at the α–α_2 transition, resembling the behaviour of Na_2WO_4 at the β–α transition. The (highest) α_2-phase is hexagonal, ($P6_3/mmc$), showing large anisotropic thermal vibrations. The α-phase is orthorhombic ($Fddd$) as is the β-phase (probably $Pbn2_1$).

The High Temperature Behaviour of In_2O_3. J. H. W. DEWIT. Inorganic Chemistry Department, University of Utrecht, Croesestraat 77a, Utrecht, The Netherlands. The electrical conductivity of In_2O_3 has been measured up to 1400°C in air. The temperature dependence of the conductivity at high temperatures yields an activation energy of 1.5 ± 0.1 eV. This activation energy is interpreted in terms of a nonstoichiometric decomposition of the compound. This interpretation is sustained by thermogravimetric analysis in combination with a gas mass analyser. Hall experiments on quenched samples are not in contradiction with this interpretation.

Filiation Structurale des Phases Derivées de $BaFeF_5$. J. RAVEZ, R. VON DER MÜHLL, AND, P. HAGENMULLER. Service de Chimie Minérale Structurale de l'Université de Bordeaux I, C.N.R.S. 351 cours de la Libération, 33405 Talence, France. The $BaFeF_5$, $Sr_3(FeF_6)_2$ and $Sr_5T_3F_{19}$ ($T =$ Ga, Cr, Co) structures are narrowly related: the octahedral chains of the $BaFeF_5$ structure can be replaced partially or completely by rows of ($1Sr^{2+} + 2F^-$) units leading to $Sr_3(FeF_6)_2$ or $Sr_5T_3F_{19}$ phases. The existence of solid solutions within the ternary system SrF_2–BaF_2–FeF_3 is explained in structural terms.

Influence de Divers Types de Substitutions Cationiques sur les Proprletés Dielectriques de Niobates de Structure "Bronzes Oxygenes de Tungstene Quadratiques." M. POUCHARD, J. P. CHAMINADE, A. PERRON, J. RAVEZ, AND P. HAGENMULLER. The value of the ferroelectric Curie temperatures in compounds with the "tetragonal tungsten bronze structure" is related to the steric effect of large alkali or alkaline-earth cations in the lattice tunnels, to the covalency of the transition element-oxygen bonds, and to the introduction of Li^+ ions, which due to their small size are able to occupy the 9 coordination sites of the structure anistropically.

Single Crystal Structure Study of α-Ag_2HgI_4: Evidence for Anharmonic Vibration. J. S. KASPER AND K. W. BROWALL. General Electric Corporate Research and Development, Schenectady, New York 12301. X-ray diffraction intensities have been measured for two single crystals of α-Ag_2HgI_4 at 66°C using MoK_α radiation monochromated by reflection from a 022 graphite face. It is found that improvement on the simple zincblende description could be made either by considering all ions to be displaced by about 0.025 Å along tetrahedral directions or by applying existing anharmonic theory for thermal motions. Although all ions are on appropriate sites to contribute to anharmonic effects, only a single anharmonic parameter, representing a weighted difference of two individual parameters, could be evaluated. The anharmonic treatment gives substantially better agreement for critical reflections of the class $h + k + 1 = 4n \pm 1$.

IR-Spektroskopische und Rontgenographische Untersuchungen an Thiospinellmischkristallen. H. D. Lutz and H. Haeuseler. Gesamthochschule Siegen, Lehrstuhl für Anorganische Chemie, 593 Huttental-Weidenau, Paul-Bonatz-Str. 9-11, Germany. The effect of the tetrahedral and octahedral coordinated metal atoms and nonmetal atoms on the vibrational spectra of spinels is studied by investigation of mixed crystals and defect spinels like In_2S_3. The following solid solutions of chromium thiospinels and indium sulfides have been prepared and investigated by X-rays and FIR-spectroscopy: $Hg_xZn_{1-x}Cr_2S_4$(I), $ZnIn_xCr_{2-x}S_4$(II), $CdIn_xCr_{2-x}S_4$(III), $ZnCr_2Se_xS_{4-x}$(IV), α-In_2S_3(V), β-In_2S_3(VI), and $Cr_xIn_{2-x}S_3$(VII). The lattice constants of (I), (III), (IV), and (VII) obey Vegard's rule. (III) has a miscibility gap between $x = 0.3$ and $x = 1.8$. The spectroscopic behaviour of the solid solutions (all the 4 peaks of the spinel spectra split or shift) cannot be interpreted on the basis of internal vibrations of different coordination polyhedra. An explanation of the additional peaks in the spectra of the mixed crystals is given according to order of the atoms or distortion of the spinel structure.

Polymorphism and Stability of Some Sodium Cryolites to High Pressures. Carl W. F. T. Pistorius. National Physical Research Laboratory, C.S.I.R., P.O. Box 395, Pretoria, South Africa. Na_3VF_6 and Na_3TiF_6 are monoclinic cryolites at ambient conditions and transform to fcc high-temperature phases at 638.5 and 611°C, respectively. The thermal expansion parameters of Na_3AlF_6 and Na_3TiF_6 were measured to ~ 700°C. The monoclinic–cubic transition lines of Na_3AlF_6, Na_3FeF_6, Na_3VF_6, and Na_3TiF_6 were followed to 40 kbar. They rise with pressure with initial slopes and curvatures that increase with increasing crystal radius of the trivalent ion. The transition entropy appears to be $R\ln 4$ in all cases. The fcc high-temperature phases are suggested to be disordered with the fluorine atoms distributed among the 96*j* (or the 96*k*) positions of Fm3m, i.e., fourfold disorder of the XF_6 octahedra. Na_3FeF_6 and Na_3CoF_6 appear to contain the trivalent ions in the high-spin state, while Na_3NiF_6 appears to exhibit an equilibrium between high- and low-spin states. Na_3XF_6 can be expected to be less dense than the assemblage $2NaF + NaXF_4$ for trivalent ions larger than Sc^{3+}, and it is therefore improbable that Na_3LnF_6 can be synthesized at high pressure.

New Nonstoichiometric Molybdate, Tungstate, and Vanadate Catalysts with the Scheelite-Type Structure. A. W. Sleight, K. Aykan, and D. B. Rogers. Central Research Department, E. I. duPont de Nemours and Company, Wilmington, Delaware 19898. Phases of the formula $A_{1-x}\phi_xMO_4$ with the scheelite-type structure are described where ϕ represents a vacancy at the A cation site and M is Mo^{6+}, W^{6+}, and/or V^{5+}. Many different univalent, divalent, and trivalent A cations were used in this study. The phases with no defects, i.e., $x = 0$, were known except for those of the type $A^{1+}_{0.5}A^{3+}_{0.5}MO_4$ where A^{1+} is Ag or Tl and M is Mo^{6+} or W^{6+}. Phases with x greater than zero are generally new and were prepared for catalytic studies. An excellent correlation between catalytic properties and defect concentration has been observed.

X-ray Photoelectron Spectroscopic Studies of Solid Electrolytes. T. Dickinson, A. F. Povey, and P. M. A. Sherwood. School of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, United Kingdom. A study of solid electrolytes by X-ray photoelectron spectroscopy reveals that silver (I) and copper (I) compounds generally show very small shifts in electron binding energies. The complex crystal structure of the β-aluminas, however, gives rise to different cation sites which can be distinguished by this technique. Calculations of self-potential show the importance of this term for determining shifts. The possibility of determining the partial ionic charge from the measured shift is also considered.

Synthése sous Haute Pression d'Oxygène d'une Forme Dense Ordonée $FeVO_4$ et Mise en Evidence d'une Variété Allotropique de Structure $CrVO_4$. J. Muller and J. C. Joubert. Laboratoire des Rayons X, B. P. No. 166—Centre de Tri, 38042—Grenoble Cedex, France. A new dense form of iron vanadate