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Abstracts of Forthcoming Articles

Etude structurale du conducteur anionique $Bi_{0.765}Sr_{0.235}O_{1.383}$. Pierre Conflant, Jean-Claude Boivin, and Daniel Thomas, Laboratoire de Cristallochimie, Université des Sciences et Techniques de Lille, 59655 Villeneuve D'Ascq Cedex, France. The structure of an O^{2-} conductor, the rhombohedral ($a = 9.75$ Å, $\alpha = 23.49°$) low-temperature form of the solid solution $Bi_{1-x}Sr_xO_{1.5-x/2}$ ($x = 0.235$, $Z = 3$) has been solved in space group $R\bar{3}m$ by means of Fourier synthesis and least-squares refinements. Intensity data were corrected for absorption. The final R value is 0.030 for 302 independent planes. Most of the bismuth atoms are located on a first set with a distorted tetrahedral coordination while the remaining bismuth and the strontium atoms are distributed on a single position with an eightfold $(6+2)$ oxygen coordination. Two types of anionic sites are detected within the tetrahedral voids of the cations sheets stacked along the [111] axis. This results in a layered structure, with loosely bound oxide ions, providing a basis for the interpretation of the ionic conductivity of the phase.

Defect Structures in the Brannerite-Type Vanadates. II. Mechanism of the Solid-State Synthesis of $Mn_{1-x}\phi_xV_{2-2x}Mo_{2x}O_6$ $(0 \leqslant x \leqslant 0.33)$. Jacek Ziòłkowski, Roman Kozłowski, Drzysztof Mocała, and Jerzy Haber, Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek, 30-239 Kraków, Poland. The mechanism of solid-solid reactions in three-component mixtures (Mn_2O_3, V_2O_5, MoO_3) has been studied by X-ray and thermogravimetric methods. The synthesis of $Mn_{1-x}\phi_xV_{2-2x}Mo_{2x}O_6$ solid solutions proceeds along three main reaction paths: (a) direct formation from oxides due to efficient surface diffusion of MoO_3 and V_2O_5 over Mn_2O_3 grains, (b) formation of $MnMoO_4$ followed by its reaction with V_2O_5 and dilution of the obtained phase with V_2O_5 and Mn_2O_3, (c) reaction of preformed MnV_2O_6 and $MnMoO_4$ with V_2O_5. The contribution of the above paths to the overall reaction depends on the composition of the initial mixture (x), temperature, and surface area of Mn_2O_3. If the synthesis of a single-phase solid solution in an MoO_3-poor region ($x < 0.20$) is aimed at, thermal treatment parameters should be selected in such a way as to exclude the preformation of MnV_2O_6 which, once formed, is not subsequently consumed to the equilibrium phase.

Layer structure: The oxides $A_3Ti_5MO_{14}$. M. Hervieu, H. Rebbah, G. Desgardin, and B. Raveau, Laboratoire de Cristallographie et Chimie du Solide, Université de Caen, 14032 Caen Cedex, France. Five new oxides—$K_3Ti_5MO_{14}$, $Rb_3Ti_5MO_{14}$ ($M = $ Ta, Nb), and $Tl_3Ti_5NbO_{14}$—have been synthesized. The structure of these oxides consists of octahedral layers which are similar to those observed for $Na_2Ti_3O_7$ and are held together by monovalent ions; the sheets consist of blocks of 2×3 edge-sharing octahedra, which are then joined to each other by the corners of the octahedra. The relative disposition of the layers is similar to that observed for $Tl_2Ti_4O_9$. These oxides can be considered as the member $n = 3$ of a series of closely related structures with formula $A_nB_{2n}O_{4n+2}$, where n indicates the number of octahedra which determines the width of the blocks of $2 \times n$ octahedra.

Effects of Additions of TiO_2, SnO_2, Ga_2O_3, *and MgO on the Phase Equilibria, Stoichiometry, and Lattice Parameter of* $Ni_{0.89}Fe_{2.11}O_4$. P. K. Gallagher, D. W. Johnson, Jr., H. Schreiber, Jr., and E. M. Vogel, Bell Laboratories, Murray Hill, New Jersey 07974. Additions up to a mole fraction of 0.1 of TiO_2, SnO_2, Ga_2O_3, and MgO were made to $Ni_{0.89}Fe_{2.11}O_4$. Pellets were equilibrated in O_2, 0.1% O_2 in N_2, and N_2 at 1150, 1250, and 1350°C. Chemical and microstructural analysis enabled the determination of phase boundaries and the mechanisms of charge compensation. Charge compensation for the solubility of the additives in the spinel was predominantly (70%) by Fe^{2+} formation, as opposed to cation vacancy formation, under the more oxidizing conditions and approached 100% under the reducing conditions. Variations in the lattice parameter of the spinel were noted as a function of additive, vacancy, and Fe^{2+} concentrations.

Phase Equilibria in the System between NbO_2 *and* Nb_2O_5 *at High Temperatures.* Keiji Naito, Naoki Kamegashira, and Norio Sasaki, Department of Nuclear Engineering, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan. Isothermal electrical conductivity measurements on niobium oxides were carried out over the temperature range from 1010 to 1300°C as a function of oxygen partial pressure in order to clarify the phase relations. Existence regions of the intermediate oxide phases between NbO_2 and Nb_2O_5 were found from the discontinuities in electrical conductivity curves. These oxide phases were also analyzed by a gravimetric method and by X-ray diffractometry. From these results the phase diagram for this system is proposed. The defect structures of these phases are also discussed.

Magnetochemical Properties of Tetranuclear Rhodoso and Pfeiffer Chromium(III) Complexes in a Series of Compounds. Hans U. Güdel and Urs Hauser, Institut für anorganische und physikalische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland. Seven salts of the structurally related tetranuclear rhodoso and Pfeiffer chromium(III) complexes were prepared. Magnetic susceptibilities were measured and the energy splittings of the electronic ground state caused by exchange interactions were determined. There are marked differences in the low-temperature magnetic properties. Crystal packing and hydrogen bonding effects are the most likely causes for the differences in the exchange-splitting pattern.

Polymorphic Transformations of Bi_2MoO_6. A. Watanabe and H. Kodama, National Institute for Researches in Inorganic Materials, 1-1 Namiki, Sakura-mura, Niihari-gun, Ibaraki, 305 Japan. The polymorphism of Bi_2MoO_6 has been studied by differential thermal analysis, differential dilatometry, and differential scanning calorimetry with γ-form specimens having the koechlinite structure prepared by sintering the oxides Bi_2O_3 and MoO_3. Two stable γ and γ' forms and one metastable γ'' form were observed. The relative thermal stability of the γ form compared with the γ' form has been examined by isothermal heating of a mixture of the two forms under hydrothermal conditions. Thus the low-temperature stable γ form transformed reversibly to the γ'' form at 604 ± 3°C, and on subsequent heating, the γ'' form transformed irreversibly to the high-temperature stable γ' form in the range 640 to 670°C, depending on heating rates; however, an isothermal treatment at a temperature above 604 ± 3°C brought the gradual transition of the γ'' form into the γ' form.

The Isotropic Temperature Factors of $Sr(Co_{1-x}Mn_x)O_3$ ($x = 0, 0.1, 0.5, 0.8$ *and* 1.0). H Taguchi, M. Shimada, M. Koizumi, and F. Kanamaru, The Institute of Scientific and Industrial Research, Osaka University, Osaka 565, Japan. The cubic perovskite $Sr(Co_{1-x}Mn_x)O_3$ has a maximum value of a-axis at $x = 0.3$ and a change of spin state of Co^{4+} ion from low to high. To elucidate these properties, the isotropic temperature factor (B) of strontium, cobalt, manganese, and oxygen atoms for $x = 0$, 0.1, 0.5, 0.8, and 1.0 have been derived from powder X-ray diffraction measurements. The isotropic temperature factor of oxygen for $x = 0$, 0.1, and 1.0 is small and that for $x = 0.5$ and 0.8 is large. This fact suggests that the oxygen ion deviates from the centre of the Co–O–Mn bond in the solid solutions with $x \geqq 0.3$. Larger CoO_6 octahedra and smaller MnO_6 octahedra, which are connected by corner sharing of oxygens of the octahedron, are distributed statistically.

Self-Diffusion of Yttrium in Monocrystalline Yttrium Oxide: Y_2O_3. R. J. Gaboriaud, Laboratoire du Métallurgie Physique, 40, Avenue du Recteur Pineau, 86022 Poitiers, France. Yttrium self-diffusion in monocrystalline yttrium oxide (Y_2O_3) is studied by means of the classical radiotracer technique. The few reliable diffusion data obtained in the temperature range 1600–1700°C lead to the diffusion coefficient $D = 3.5 \times 10^9 \exp - (72/RT)(\mathrm{kcal/mole})\ \mathrm{m}^2\ \mathrm{sec}^{-1}$. Experimental errors on the above numerical values are large and give, for the preexponential and energy terms, respectively, $2 \times 10^{-7} < D_0 < 3 \times 10^{-10}\ \mathrm{m}^2\ \mathrm{sec}^{-1}$ and $62 < Q < 82$ kcal/mole. Nevertheless these results seem in good agreement with those deduced from high-temperature and low-stress creep experiments. The theoretical aspect of self-diffusion of yttrium in Y_2O_3 is studied in terms of point defects and lattice disorder due to the equilibrium between the oxide and its environment. This last part is confined to the restricted range of high oxygen partial pressure in which oxygen interstitials are supposed to be majority defects. Intrinsic and extrinsic diffusion behaviors are both considered on the basis of a vacancy diffusion mechanism.

Study of $Pr_{1-x}Mn_{1+x}O_3$ *Perovskites.* Emil Pollert and Zdeněk Jirák, Institute of Physics, Czechoslovak Academy of Science, Na Slovance 2, 180 40 Praha 8, Czechoslovakia. The structural and magnetic properties of the $Pr_{1-x}Mn_{1+x}O_3$ perovskites were studied. The increase of x (i.e., $Pr/Mn < 1$)