

which are linked along edges and/or corners. However, as the linkage parallel to b takes place only by sharing corners, an anisotropy in the electrical conductivity may be expected. Another explanation for the smaller conductivity may be found in the occurrence of defects such as tunnels in the structure, which may scatter the electrons. The refinement shows that the tungsten positions, determined by Magneli (1949), are essentially correct; but the positions of the oxygens, especially two of them, differ considerably. This results in one of the tungsten atoms getting an additional coordinating oxygen, the coordination number thereby becoming 7.

Structure de SnPb_2O_4 a Quatre Temperatures Relation Entre Dilatation et Agitation Thermiques. J. R. GAVARRI, J. P. VIGOUROUX, G. CALVARIN AND A. W. HEWAT, Laboratoire de Chimie-Physique du Solide, Ecole Centrale, 92290 Chatenay Halabry, France. The structural study of SnPb_2O_4 oxide, an isomorphous compound belonging to the general family " MeX_2O_4 " like Pb_3O_4 , is made from accurate X-ray and neutron diffraction techniques on powdered samples. The structural evolution of SnPb_2O_4 is analyzed from 300 to 5 K: no phase transition is observed contrary to Pb_3O_4 which exhibits a quadratic \rightarrow orthorhombic transition at 170 K. The thermal expansion tensor is practically isotropic in this temperature range: the α_a and α_v coefficients are neighboring those observed in the Pb_3O_4 tetragonal phase at the same temperature. On the other hand, the thermal vibrations are strongly anisotropic, with large amplitudes in the (a, b) plane. In this study we connect the thermal vibrations to the thermal expansion. $\bar{B}ab$ and $\bar{B}c$ temperature factors are considered as functions on the a and c cell parameters. We discuss the relation established by Gruneisen between the mean square amplitudes of vibrations and the thermal volume expansion. The interatomic distances we found show that the bindings are similar to that of Pb_3O_4 : only the $[\text{Sn}^{4+}\text{O}_6]$ octahedra are smaller than $[\text{Pb}^{4+}\text{O}_6]$ octahedra.

The Phase Relations in the Binary System of TiO_2 - Na_2O by the Hydrothermal Reactions of TiO_2 with NaOH . MAMORU WATANABE, National Institute for Researches in Inorganic Materials, Namiki 1-1, Sakura-mura, Niihari-gun, Ibaraki, 300-31, Japan. The hydrothermal reactions of TiO_2 with NaOH were performed in the molar range of Na_2O from 0 to 30% between 250 and 530°C. The compounds obtained are TiO_2 (rutile, brookite, and anatase), $\text{Na}_2\text{O} \cdot n\text{TiO}_2$ ($n = 3, 4, 6$, and 9) and Na_xTiO_2 , of which the formation ranges are shown in a reaction diagram. The roles of water in this hydrothermal system are investigated to discuss the differences among the known and the present reaction diagrams and to raise a reliability of diagrams. From the present reaction diagram, phase relations in the system TiO_2 - Na_2O are estimated taking account of the direct or indirect actions of hydrothermal water on solid phases.

Structural Aspects of the Metal-Metal Interactions in the $\text{Ti}_{1+x}\text{S}_2$ Materials. E. TRONC AND R. MORET, Laboratoire de Chimie Appliquée de l'Etat Solide, ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris Cédex 05, France. Interlayer metallic interactions are shown to manifest themselves in both stacking correlations and titanium sublattice distortions. A quantitative study is reported through the structure refinement of one of the $\text{Ti}_{1.33}\text{S}_2$ superstructures. The interactions seem to involve Coulomb repulsion forces and should be valid in a broad composition range. Lattice distortions are predicted for other structures including the nonstoichiometric 1T structure.

Crystallography and Phase Relations of $\text{MeO-M}_2\text{O}_3\text{-TiO}_2$ Systems ($\text{Me} = \text{Fe, Mg, Ni}$; $\text{M} = \text{Al, Cr, Fe}$). J. HAUCK, Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, Federal Republic of Germany. Subsolidus phase relations of ternary oxide systems containing divalent Fe, Mg, or Ni; trivalent Al, Cr, or Fe; and tetravalent Ti are characterized by solid solutions at metal/oxygen ratios $\frac{2}{3}$, $\frac{3}{4}$, and $\frac{3}{5}$. At low temperatures only compounds with cubic or hexagonal close-packed oxygen and uniform oxygen coordination remain stable in the crystal structures: NaCl, spinel, ilmenite- $\alpha\text{-Al}_2\text{O}_3$, TiO_2 . The pseudobrookite phases FeTi_2O_5 , MgTi_2O_5 , Al_2TiO_5 , Fe_2TiO_5 ; the V_3O_5 -structure phase Cr_2TiO_5 ; and the Andersson phases $\text{Cr}_2\text{Ti}_{n-2}\text{O}_{2n-1}$ ($n = 4, 6, 7, 8, 9$) decompose. Additional phases with close-packed oxygen as predicted by a simple structure model for metal/oxygen ratios $\frac{1}{2}$, $\frac{3}{4}$, and $\frac{1}{2}$ do not form but presumably are important for nonstoichiometric solid solutions. Most differences between systems containing transition metals and the $\text{MgO-Al}_2\text{O}_3\text{-TiO}_2$ system can be attributed to crystal field effects.

Magnetic Resonance Study of $(\text{Gd}_x\text{Y}_{1-x})\text{Co}_2$ Compounds. E. BURZO, MAGDA BALANESCU, AND M. CHIPARA, National Center of Physics, P.O. Box 5206, Bucharest, Romania. The results of magnetic resonance studies on ferrimagnetic $(\text{Gd}_x\text{Y}_{1-x})\text{Co}_2$ compounds, both below and above the Curie points,

are presented. The ferrimagnetic resonance measurements show that the effective g values can be described by using the Wangness relation. The spectroscopic splitting factors of cobalt atoms are not composition dependent. In the paramagnetic range the thermal variation of the linewidth is not linear and the g values are a function of temperature. This behavior is analyzed with respect to the magnetic data.

Crystal Chemistry of the $(\text{Ta}_6\text{Si}_4\text{O}_{26})^{6-}$ and $(\text{Ta}_{14}\text{Si}_4\text{O}_{47})^{8-}$ Frameworks. D. P. BIRKETT, P. J. WISEMAN, AND J. B. GOODENOUGH, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, England. The range of chemical flexibilities of the hexagonal frameworks $(\text{Ta}_6\text{Si}_4\text{O}_{26})^{6-}$ and $(\text{Ta}_{14}\text{Si}_4\text{O}_{47})^{8-}$ has been partially explored. This has been done with high-temperature preparations as, in general, ionic mobilities in these frameworks are too low to permit low-temperature ion exchange. Ionic site potential calculations indicate that preferential site-occupancy factors as well as geometric constraints are responsible for the absence of ionic motion. New phases $\text{K}_{6-x}\text{Na}_x\text{Ta}_6\text{Si}_4\text{O}_{26}$ ($x \leq 4$), $\text{K}_{8-x}\text{Na}_x\text{Ta}_{14}\text{Si}_4\text{O}_{47}$ ($x \leq 5$), and impure $\text{Ba}_{3-x}\text{Na}_{2x}\text{Ta}_6\text{Si}_4\text{O}_{26}$ have been prepared. Introduction of up to 2 moles of Li^+ and 1 mole of Mg^{2+} ions per formula unit into sites of the framework not normally occupied has been demonstrated as well as the possibility of partially substituting Zr^{4+} for Ta^{5+} ions. Substitutions designed to introduce large tunnel vacancies in the presence of only monovalent K^+ or Na^+ ions (P for Si, W for Ta, and F for O) generally proved unsuccessful. Competitive phases also frustrated attempts to substitute either the larger Rb^+ or the smaller Li^+ ions into the large tunnel sites. A large area of solid solution was discovered in the $\text{BaO}-\text{Na}_2\text{O}-\text{Ta}_2\text{O}_5$ phase diagram; it has a $(\text{TaO}_3)^-$ framework with the structure of tetragonal potassium tungsten bronze.

Structure Cristalline de NaBaPO_4 . A. W. KOLSI, M. QUARTON, AND W. FREUNDLICH, Université Pierre et Marie Curie, Laboratoire de Chimie Minérale, Tour 54, 2e étage, 4, place Jussieu 75230 Paris Cédex 05, France. Crystal preparation of NaBaPO_4 ; space group: $C2/m$; cell dimensions: $a = 9.743(3)$, $b = 5.622(1)$, $c = 7.260(1)$, $\beta = 90.10(3)^\circ$, $Z = 4$. The main characteristic of the NaBaPO_4 structure consists of a statistical occupation of some special positions ($4i$) by Na or Ba atoms. The network is built up with PO_4 tetrahedra, NaO_6 octahedra, BaO_{12} and MO_{10} polyhedra ($M = \text{Na}$ or Ba). The final R value is 0.058.

Tunnel and Intergrowth Structures in the Gallia-Rich Gallium Titanate System. L. A. BURSILL AND G. G. STONE, School of Physics, The University of Melbourne, Parkville, 3052, Australia. Phase analysis studies of the homologous series $\text{Ga}_4\text{Ti}_{m-4}\text{O}_{2m-2}$ by electron microscopy and diffraction reveal that $m = 5$ and 7 may occur but they are metastable, appearing only in incompletely reacted specimens. Thus $m = 9$ is the lowest stable member of the series. The observation of and structure determination of a new tetragonal tunnel structure, containing hollandite-type tunnels separated by elements of the β -gallia and rutile structure types, is also reported. The stoichiometry range $M_x\text{Ga}_{10+2x}\text{Ti}_{6-2x}\text{O}_{27}$ ($M = \text{Al}_2\text{O}_3^{2+}$; $0.80 < x < 1.20$) is suggested for this phase, since Al^{3+} is necessary to stabilize this phase. Lattice image studies of Ga_2TiO_5 reveal that it does not have the pseudobrookite structure, as assumed by previous authors, but instead adopts the "low-temperature" Ti_3O_5 structure type.

Un Nouveau Matériau, Ag_9GaSe_6 : Etude Structurale de la Phase α . JEAN-PIERRE DELOUME AND RENÉ FAURE, Laboratoire de Chimie Analytique II, Université Claude Bernard-Lyon I, 43 Boulevard du 11 November 1918, 69622 Villeurbanne Cédex, France. α - Ag_9GaSe_6 is cubic, space group $F\bar{4}3m$, with $a = 11.126(2)$ Å and $Z = 4$. The diffraction pattern at 20°C using $\text{MoK}\alpha$ radiation was collected with an automatic four-circle diffractometer. The structure was determined by beginning from the low-temperature structure (β - Ag_9GaSe_6). An anisotropic full-matrix least-squares refinement was performed yielding a final R of 0.063 for the 103 reflections actually measured. The 4 Ga atoms and 8 Se atoms are located on a $16(e)$ position. All the Ga-Se bonds are $2.366(10)$ Å. The Ag atoms are equally distributed on three sets of positions: two $48(h)$ and one $96(i)$. Among the 36 Ag atoms, 24 are bound to 3 Se atoms in an almost planar triangular arrangement [$2.43(4) < \text{Ag}-\text{Se}$ bonds $< 2.85(7)$ Å], and 12 are in a tetrahedron of 4 Se atoms [$2.68(5) < \text{Ag}-\text{Se}$ bonds $< 2.93(5)$ Å].

Electrochemistry of $\text{Na}_2\text{SO}_4(\text{I})$ Solid Solutions with Aliovalent Cation Substitution. H. H. HOFER, W. EYSEL, AND U. VON ALPEN, Institut für Kristallographie, Technische Hochschule, D-5100 Aachen, Germany. Conductivity data of several $\text{Na}_2\text{SO}_4(\text{I})$ solid solutions with cation substitutions are presented. The substitution of sodium by bi- and trivalent atoms generates cation vacancy concentra-