

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-

tions up to 30% in the structure of $\text{Na}_2\text{SO}_4(\text{I})$, thus creating high mobility of Na^+ . Electrochemical measurements showed that Na^+ ion conductivity prevails and that the electronic partial conductivity is negligible. Complex impedance diagrams were used to determine the influence of the vacancy concentration on the ionic conductivity of $\text{Na}_2\text{SO}_4(\text{I})$ solid solutions. It was found that the conductivity is strongly correlated to the vacancy concentrations, whereas the size and the charge of the substituting ions show no effect within the accuracy of the measurements. The activation energy as a function of the vacancy concentration exhibits a minimum of 0.7 eV at a vacancy concentration of 1%. The maximum of conductivity was found to be $1.5 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 500°C with 7% vacancies.