07.3-4   X-RAY AND NEUTRON POWDER DIFFRACTION STUDIES OF NASICON SUPERION CONDUCTORS. By A. Clearfield, A. Moini, P.R. Rudolf and J.D. Jorgensen, Department of Chemistry, Texas A&M University, College Station, Texas and Argonne National Laboratory, Argonne, Illinois, U.S.A.

NASICON is the generic name for a family of superion conductors for which the general formula, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, has been proposed (H. Y.-P. Hong, Mat. Res. Bull., 1976, 11, 173-179). We have prepared NASICONs by a variety of methods (high temperature, solid state reactions, sol-gel and hydrothermal techniques) and determined their stoichiometry and structure using analytical procedures and X-ray and neutron powder diffraction methods. The above formula is inadequate to decribe the stoichiometry and an expanded one, $Na_{1+x+4y}Zr_{2-y-z}Si_xP_{3-x}O_{12-2z}$, is required. Furthermore, the monoclinic to rhombohedral phase transition was found not to occur based upon high-resolution neutron diffraction studies in the temperature range 143-391°C. An alternative explanation for the change in slope of the conductivity curve at 180°C will be presented. Evidence will be presented to show that the preparations are path dependent and exhibit differences in composition and structure resulting from the different synthetic methods.

07.3-5   MODULATED STRUCTURE IN A Bi_2O_3-Nb_2O_5 SYSTEM. By R. Miida, S. SUZUKI and M. TANAKA, Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan.

The existence of a modulated structure in a fluorite-type fast-ion-conductor $(Bi_2O_3)_{1-x}(Nb_2O_5)_x$ $(0.13 \leq x \leq 0.24)$ was found. Fig. 1 shows an electron diffraction pattern obtained from a $(Bi_2O_3)_{0.76}(Nb_2O_5)_{0.24}$ specimen. Strong spots such as indicated with the indices are fundamental reflections expected from the fluorite structure, and the other weak spots are due to a lattice modulation. Their intensities increases as x increases. Fig. 2 shows the ratio, k/k_{111} as a function of x, where k and k_{111} are the wave number vectors of the satellite spot indicated by an arrow and the 111 spot, respectively. This clarifies that the period of the modulation wave decreases from $2.78d_{111}$ to $2.61d_{111}$ (d_{111}=the spacing of the (111) plane), when x increases from 0.13 to 0.24. Crystal structure images revealed that no incommensurate wave but a mixture of two commensurate waves with the periods of $2d_{111}$ and $3d_{111}$ exists. A fairly good agreement between the mean period of the mixture and $d/d_{111}(=k_{111}/k)$ is obtained.
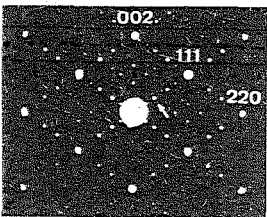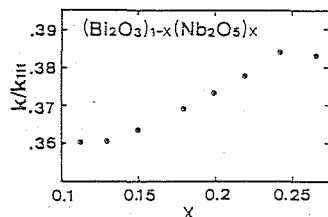

Fig. 1

Fig. 2

07.3-6   CATION ORDERING, DOMAINS AND CONDUCTIVITY IN SOME HOLLANDITE IONIC CONDUCTORS. By E. Fanchon, J. Vicat, J.L. Hodeau, J.P. Lévy and P. Wolfers, Laboratoire de Cristallogaphie, associé à l'U.S.T.M.G., C.N.R.S., 166 X, 38042 Grenoble Cedex (France).

Hollandite-type compounds $A_x(B_{8-y}B'_y)O_{16}$ with tunnels partially filled by A-cations are of considerable interest for the elucidation of superionic conduction.

Depending on the A, B or B' cations, diffraction patterns of the compounds present either diffuse planes perpendicular to the tunnel direction or superstructure reflections. The first compounds are superionic conductors, and we measured the conductivity for crystals with A = K+, corresponding to different x values and different substitutions of B and B' framework cations. Compounds with ordered superstructures, such as $Ba_{1.33}(Ti,Mg)_8O_{16}$, are not good ionic conductors. However the superlattice informations can be used to gain insight into ordering of A cations/vacancies and B/B' cations.

Diffraction patterns for $Ba_xTi_{8-x}Mg_xO_{16}$ (x ≈ 4/3) exhibit satellites which are not exactly commensurate with the sublattice peaks along the b-tunnel direction. These compounds are monoclinic, pseudo-tetragonal. The commensurate $q^* = 0.33 b^*$ superstructure can be described by a 3 fold supercell along b (whereas the periodicity is unaffected along a and c : a = 10.245(1), b = 8.940(4), c = 9.924(1) Å, ß = 91.00(1)°, space group P2/n). X-ray data refinements lead to the Ba-Ba-□ ordered sequence, the Ba-cations being displaced along the channel from the center of the site. As in $Ba_{1.2}Ti_{6.8}Mg_{1.2}O_{16}$ (Fanchon et al., Acta Cryst. B, to be published), refinements taking into account domain which correspond to Ba/□ sequences translated by 1 or 2 subcells relative to the reference matrix give improved results. For our crystal, x seems smaller than 1.33 and incommensurate models are currently being tested. Results do not reveal any Ti/Mg ordering in the framework.

The other compounds studied here exhibit diffuse planes characterized by modulation vector q^*, indicating small correlation between tunnels as in the well-known $K_{1.54}(Ti,B')_8O_{16}$ compounds (B' = Mg, Al). By direct synthesis and flux methods, large crystals have been synthetized with the following formula : $K_{2x}Ti_{8-x}Zn_xO_{16}$, $K_{2x}Sn_{8-x}Zn_xO_{16}$, $K_{2x}Ti_{8-2x}Ga_{2x}O_{16}$ and $K_{2x}Sn_{8-2x}Ga_{2x}O_{16}$. From the $q^* = 1-x$ relation (Mijlhoff et al. (1985), Acta Cryst. B41, 98-101), the 2x values are 1.54 and 1.60 for Ti compounds and 1.80 for the Sn phases. Single crystal conductivity measurements are presented and discussed.