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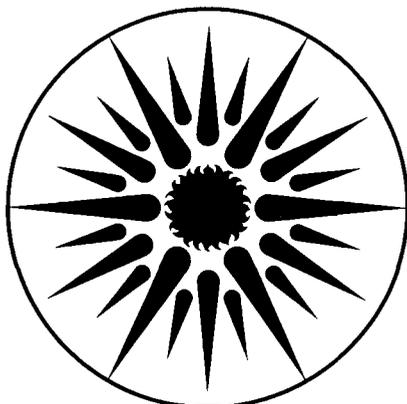
PRINCIPLES OF SUPERIONIC CONDUCTION
Annual Summary Report for 1982

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PRINCIPLES OF SUPERIONIC CONDUCTION*

Annual Summary Report for 1982

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Submitted to:

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Alkali-ion conductors of relevance to battery systems and other solid-electrolyte applications have been examined in the present program in an attempt to gain insight into the principles which govern fast-ion conduction. The program has two main tasks:

(a) Performing exploratory syntheses, characterization, and conductivity measurements of possible new fast-ion conductors. Such phases include members of new structural families whose characteristics suggest a high likelihood for fast-ion conduction, but for which property measurements have not been performed. Also under study are crystal-chemical modifications of structures already known to be good conductors.

(b) Determination of crystal structures, using x-ray or neutron scattering, of materials of high conductivity and in which a marked variation of property with structure and chemistry is apparent. The objective is to establish the locations, site occupancies and thermal vibration amplitudes of the mobile ions, and to relate transport properties to changes in framework geometry and changes in the atomic arrangement at the saddle point of likely diffusion jumps. Such structure-property relations are an essential basis of the understanding which will permit the tailoring of new compositions with desirable properties.

The ionic electrical conductivity of solid solutions in the NASICON solid solution system, $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, is known to increase to a maximum ($0.2 \text{ ohm}^{-1}\text{cm}^{-1}$ at 300°C) at $x = 2.3$, a value four orders of magnitude larger than the conductivity of the end-members of the system. The increase in conductivity seemed closely connected to structural change as one lattice constant and the unit cell volume of the solid solutions pass through a maximum near the same composition. The structural change, moreover, is anomalous in that the cell volume would be expected to expand monotonically with increasing replacement of P by the larger Si ion. No structural data was available for an intermediate solid solution in the NASICON system or any other related system. The distribution of Na among available sites, the ordering (if any) of Si and P, the structure of the monoclinic phase which occurs for $1.6 < x < 2.2$ and its relation to the rhombohedral structure at other x , were all consequently unknown and greatly limited insight into the transport mechanism in these phases.

Detailed structural analyses of a series of solid solutions extending across the NASICON system [$x = 1.0$ and 2.5 (hexagonal, $R\bar{3}c$) and $x = 1.6$ and 2.0 (monoclinic, $C 2/c$)] have been completed in the past year. Rietveld profile analysis was performed with powder diffraction data collected in 0.05° 2θ steps for $12^\circ < 2\theta < 117^\circ$ with Cu-monochromated 1.5423 \AA neutrons. Least-squares refinement of the structural parameters proceeded to highly satisfactory weighted profile residuals which ranged 6.45-8.38% for the four

compositions, values close to residuals of 5.07-5.28% expected on the basis of counting statistics. Of two available sites for the mobile Na ions, a first which is fully occupied at $x = 0$ was found to remain fully occupied at all compositions. A second site, Na(2), found fully occupied at $x = 3$, fills progressively with increasing x . In the monoclinic phases, Na(2) splits into two sets of symmetry-independent sites which are not equally occupied. Extrapolation indicates that these will have equal occupancy (i.e., equal energy) at $x = 2.1$, a composition close to that of maximum room temperature conductivity. The Si and P ions were found to be ordered (but not fully) in both monoclinic phases. Both Na(1) and Na(2) have highly anisotropic values of the parameters necessary to describe their thermal vibrations, maximum displacement occurring normal to the c axis (or pseudo-hexagonal c axis) and nearly parallel to c for the two ions, respectively. The thermal motion for Na(1) was found to be only apparent, however, as Fourier synthesis of the scattering density for this ion revealed it to be displaced to locations off the center of its coordination octahedron.

The principal change in the framework with change in composition is distortion and rotation of the orientation of the Si/P tetrahedra as x increases to 2.0, followed by progressive return toward the original orientation for larger x . This rotation acts to increase the height of the Na(1) octahedron along C_{HEX} and is

responsible for the anomalous maximum in the value of c as a function of composition. A procedure for calculation of the position and maximum radius of the sphere which can just pass through a non-coplanar assemblage of rigid equal spheres was developed and used to evaluate the size of the "window" at the saddlepoint for jumps along likely Na diffusion paths in the structure. It is found that the rotation of the tetrahedral units in NASICON causes the windows to increase to a maximum size, close to the radius of Na^+ , near $x = 2$, the composition of maximum conductivity.

The probable diffusion path which is responsible for the high ionic conductivity of NASICON is likely a jump between Na(2) sites. This view is supported by (a) highly anisotropic thermal vibration (and thus a softer potential energy well) in a direction along the line connecting such sites (the apparent anisotropy of Na(1) vibrations actually representing an average of positional disorder), (b) the correspondence between the composition of maximum room temperature conductivity and that at which the site energies of these locations become equal and (c) the fact that the product of Na charge carriers and vacancy concentration, $C(1-C)$, which obtains maximum value at $C = 1/2$, coincides with maximum observed conductivity when C is taken as the Na(2) concentration rather than the total Na concentration.

The ionic conductivity of solid solutions in the NASICON system therefore reaches a maximum for intermediate compositions

because the concentration of Na ions and the window size along the diffusion path both reach optimum values near the same composition.

(The fact that the energies of non-equivalent Na(s) sites in the monoclinic phases also become equal near this composition would also contribute to the enhancement of the room-temperature conductivity. This would not be a factor at the elevated temperatures at which these phases have transformed to the rhombohedral structure in which all Na(2) sites are symmetry-equivalent.)

The relevance of these results toward the development of improved battery materials is that information on the diffusion mechanism, as well as the window size and Na concentration necessary for optimum conduction, have now been established. Accordingly, it should be possible on this basis to use known interionic distances to tailor new compositions with similar structural parameters including some, perhaps, which might be free of the phosphorus component which has been suggested as the origin of degradation of NASICON in the presence of molten sodium.

Presentations

I. Kohatsu, A. K. Ekholm and B. J. Wuensch, "Electrical Conductivity of Some NASICON-Related Solid Solution Systems". 84th Annual Meeting, American Ceramic Society, Cincinnati, May 4, 1982. [Bull. Am. Ceram. Soc. 61, 419 (1982).]

L. J. Schioler, B. J. Wuensch and E. Prince, "Structural Changes in the NASICON Solid Solution System". Fall Meeting, Basic Science and Electronic Division, American Ceramic Society, Cambridge, Mass., September 13, 1982. [Bull. Am. Ceram. Soc. 61, 805 (1982).]

B. J. Wuensch, "Relation of Structure and Conductivity in the NASICON Solid Solution System". Research Assistance Task Force Meeting on β -Al₂O₃ for Sodium/Sulfur Batteries, Office of Energy Systems Research and Office of Basic Energy Science, U.S. Department of Energy. Oak Ridge National Laboratory, March 9, 1983.

L. J. Schioler, B. J. Wuensch and E. Prince, "Neutron Rietveld Analysis of Structural Changes in the Fast-Ion Conducting NASICON Solid Solution System, Na_{1+x}Zr₂Si_xP_{3-x}O₁₂". Paper PC5, Winter Meeting, American Crystallographic Association, Columbia, Missouri, March 17, 1983.

L. J. Schioler, B. J. Wuensch and E. Prince, "Structure-Conductivity Considerations in NASICON", 85th Annual Meeting, American Ceramic Society, Chicago, April 27, 1983. [Bull. Am. Ceram. Soc. 62 [3] (1983).]

L. J. Schioler, B. J. Wuensch and E. Prince, "Relation Between Structural Change and Fast-Ion Conduction in the NASICON Solid Solution System". 4th International Conference on Solid State Ionics, Grenoble, France, July 4-8, 1983. (Paper accepted for presentation; to be published in Solid State Ionics.)

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