

that surface grinding of these materials usually leads to substantial surface compressive stresses, which should also be useful in increasing the reliability of these materials.

### Plans and technical objectives for 1983

#### *Fabrication*

-Choose fabrication route and composition that maximizes strength/resistivity ratio of these composites;

-Explore use of centrifugal casting as a technique for consolidating green ceramic bodies;

-Study techniques for producing agglomerate-free, ceramic powders containing both the zirconia and the beta"-alumina phases.

#### *Performance*

-Study behavior of material in presence of liquid sodium;

-Determine whether the composite materials are more resistant to the electrolytic degradation that occurs during the use of these materials in advanced battery systems (in conjunction with L. DeJonghe, LBL).

## FABRICATION AND CHARACTERIZATION OF NASICON SOLID ELECTROLYTES

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The objectives of this project are to fabricate Nasicon ( $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ) tubes and their quality control evaluation so as to evaluate Nasicon as an alternative to  $\beta''\text{-Al}_2\text{O}_3$  electrolyte for use in Na/S batteries.

Processing and characterization of Nasicon ceramic electrolytes have been conducted using a number of different techniques. Sintering of these materials was accomplished at temperatures between 1100 and 1375 °C. Results of this work have shown that Nasicon ceramics with compositions around  $x = 2$  (i.e.,  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ), are not monophase, possess poor mechanical strength and an anomalous thermal expansion behavior, and are subject to chemical instability in the presence of liquid sodium (at 300 °C). Using wet-chemical techniques, X-ray diffraction analysis, and scanning electron microscope (SEM) observations, it was found that Nasicon apparently exhibits phase and chemical decomposition at densification temperatures.

The products of this decomposition process can be correlated with the poor physical and corrosion-resistant properties.

An examination of Nasicon ceramics prepared at different compositions using several processing methods demonstrates that these materials undergo decomposition into their component oxides during sintering. Many, if not all, of the poor physical properties of these materials can be attributed to this decomposition phenomenon. Poor mechanical properties resulting from nonuniform particle shrinkage, microcracking, second-phase constituents, and coarse spherical voids are a direct result of the decomposition of this material. Furthermore, many of the negative results obtained during electrolytic testing of these ceramics may be attributed to the decomposition of this material during densification. Significant new developments in either the areas of processing or composition are needed before contiguous, corrosion-resistant Nasicon electrolytes can be consistently produced.

## PRINCIPLES OF SUPERIONIC CONDUCTION

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The objective of this program is to provide insight into the mechanisms of fast ion conduction in alkali ion conductors of potential relevance to battery systems. This will be done by (1) performing measurements of ionic conductivity of potential fast-ion conductors with synthesis of new structure types as well as crystal-chemical modifications of structures with demonstrated fast-ion conduction and (2) specifying probability distribution and thermal motion of the mobile ions through precise neutron scattering techniques in materials in which conduction varies markedly with composition.

### Synthesis and properties of Nasicon-related solid solution systems

A large number of phases  $Al_n^+X_2^{k+}(T^1+O_4)_3$  where  $0 < n < 4$  and  $n + 2k + 3 = 24$ , assume the Nasicon structure type. In solid solutions in which substitution is made for either the octahedral framework cation,  $X$ , or the tetrahedral cation,  $T$ , the  $C$ -axis of this rhombohedral structure and the unit cell volume typically rise through an anomalous maximum for intermediate compositions. The ionic conductivity of the mobile alkali ion, usually low or moderate for the end members, rises to a maximum at or near the same composition. It is not clear whether the change in cell volume, the concentration of mobile ions, a change in the 'window' between alkali-ion sites, or a combination of these influences is responsible for the enhanced conduction.