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THE EFFECT OF DECOMPOSITION ON THE DENSIFICATION
AND PROPERTIES OF NASICON CERAMIC ELECTROLYTES

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Abstract

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°C and 1375°C. Results of this work have shown that NASICON ceramics with compositions around $x=2$ (i.e., $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_2\text{O}_{12}$), are not monophasic, 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 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.

Introduction

The potential uses for ionic conducting solids has grown over the past few years due to an increased need for efficient energy conversion and storage. Extensive research, development and testing of various fast-ion transport materials is occurring worldwide. Much of the present work on solid state ionics was initiated by Weber and Kummer (at Ford) when they observed that sodium-beta- and beta''-alumina exhibited high sodium-ion mobility above room temperature. [1] Since that time, a wide variety of ceramic materials, glasses, and polymeric compounds have been shown to possess fast-ion transport properties. [2] Many materials have been synthesized which exhibit either mono- or divalent cation conductivity at reasonable temperatures. Additionally, several ceramic materials show good anionic conductivity. Many of these compounds will undoubtedly play vital roles as essential elements in novel devices such as thermoelectric generators, fuel cells, specific-ion probes, and metal purification and/or synthesis cells. For sodium-ion conductors, particular emphasis has been placed on their use in high performance batteries such as the sodium-sulfur battery. Announced by Ford in the late 1960's, this battery system is currently being considered for extensive use in both electromotive and load-leveling applications. [3] Since its announcement, most of the research on sodium-ion conductors has concentrated on an assessment of the properties and stability of the polymorphic sodium-aluminates. Extensive work has been conducted on the processing and characterization of these materials. [10] It is now generally recognized that both beta- and beta''-alumina, when prepared in polycrystalline form from high purity materials, exhibit long-term stability in the presence of liquid sodium and/or sodium-polysulfides. [11] These two compounds have repeatedly demonstrated their capabilities of passing significant amounts of charge for extended periods of time without undergoing substantial degradation.

Although many of the problems associated with the sodium-aluminate conductors now appear to be solved, during early development work, these same problems were considered serious. Excessive sintering temperatures, volatilization of sodium, exaggerated grain growth and inadequate phase conversion were among many of the processing difficulties encountered. Because of these problems, basic research was initiated on an investigation and development of other sodium-ion conducting ceramics. [4] The discovery and characterization of a sodium-zirconium-silicophosphate compound possessing very high ionic conductivity was a result of a portion of these studies. This material entitled NASICON (an acronym for Sodium-Super-Ionic-Conductor), has comparable conductivities to the best sodium-aluminate conductor (i.e., beta"-alumina). As reported by Hong, this material exists as a variable composition compound in accordance with the following relationship: $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, for $x=0$ to 3. [5] The best conductivities were found for compositions between $x=1.8$ and 2.4. Since Hong's original work, other sodium-ion conducting ceramics have been synthesized including $\text{Na}_5\text{YSi}_4\text{O}_{12}$ [6] and a family of NASICON materials possessing isostructural characteristics-- $\text{Na}_{1+x}\text{Zr}_{2-x}\text{M}_x\text{P}_3\text{O}_{12}$ ($x=0$ to 2, $M=\text{Y}$, Yb , and In), and $\text{Na}_3\text{Sc}_2\text{P}_3\text{O}_{12}$. [9] The conductivities of these materials are also excellent and comparable to the sodium-beta-aluminas. Unfortunately, raw material costs for the scandium and rare-earth based conductors are expected to be too high for widespread use in anything other than specialized advanced batteries. However, other uses for these more costly conductors are feasible. Only the original NASICON (i.e., $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$) appears to be economically competitive with beta"-alumina for low-cost high energy density batteries.

Unlike beta"-alumina, which is a two-dimensional conductor, NASICON possess a crystal structure which allows sodium-ion mobility in three directions. The basic structure consists of a three-dimensional network of PO_4 and SiO_4 tetrahedra corner shared with ZrO_6 octahedra.

Sodium ions occupy interstitial positions. There are two distinguishable alkali-ion sites in the structure. One site is completely occupied while a second site varies in its occupancy from zero to 100% depending upon the composition selected. The basic unit cell exhibits rhombohedral symmetry, although a small distortion to monoclinic symmetry occurs in the composition interval 1.8×2.2 .

When it was first announced, NASICON was purported to be free of the myriad of fabrication difficulties associated with the beta-aluminas. [12] Original work performed by Kafalas et. al. indicated that the fabrication of polycrystalline tubular shapes and their subsequent testing in Na-S cells appeared straight-forward. [13] Since that time, considerable effort has been expended in the areas of powder synthesis, forming, sintering, characterization, and corrosion testing of electrolyte specimens. Several independent research groups have endeavored to duplicate Kafalas' results with only sporadic success. Researchers have discovered that at compositions around $x=2$ (i.e., $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_2\text{O}_{12}$), a monophase NASICON is difficult to produce, [14-18] possesses poor strength characteristics [14-19] and an anomalous thermal expansion behavior, [16, 19-22] and is subject to chemical instability in the presence of liquid sodium (at 300°C). [14, 23] Such work has cast a gloomy shadow over the prospects for this material's use in high-temperature advanced batteries.

In the present study, an examination of the physical properties and compositional homogeneity of NASICON ceramics has been conducted. NASICON materials formulated at different starting compositions and prepared from alternative powder processing methods appear to exhibit decomposition at temperatures where densification normally occurs. Using various quantitative and qualitative measures, the mechanics of this decomposition process have been characterized and are presented and discussed.

Experimental Procedures

NASICON materials prepared and analyzed in this study ranged in composition from $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_{0.12}$ to $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$, (i.e., $x=2$ to $x=2.4$ in the formula $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$). Two different approaches were used in the preparation and fabrication of ceramic specimens. The first approach involved the mechanical mixing, calcining and milling of component oxides or oxide precursors. The second approach utilized a solution preparation method generally referred to as "gel-processing".

Mechanical Mixing Processes

Raw materials utilized in this powder synthesis route included reagent grade Na_2CO_3^* and $\text{NH}_4\text{H}_2\text{PO}_4^*$, or $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}^*$, unstabilized ZrO_2^{**} , and SiO_2^{***} . Following assaying, these materials were combined in appropriate quantities to yield the desired composition and mixed in either rubber or ceramic lined jar mills for one hour using either zirconia⁺ or alumina⁺⁺ milling media at media to powder ratios of around 10 to 1. Calcination of these mixtures was performed in a three-step operation which included intermittent holds of four hours each at 170°C followed by final firing at 1150°C for 16 hours. Comminution of the calcined powders was accomplished by either dry-ball milling⁺⁺⁺ or attrition milling[†] methods. Ball-milling was conducted for 24 to 48 hours using alumina media⁺⁺. Attrition milling was performed for a maximum of 8 hours using either zirconia^{††} or mullite^{†††} media. The media wear for each process was carefully monitored to

* J.T. Baker Co., Phillipsburg, Penn.

** Type ZYP Unstabilized ZrO_2 , Zircar Products, Inc., Florida, N.Y.

***Aerosil 200V, Degussa Products, N.Y., N.Y.

+ 1/2" cylinders, Zircoa Inc., Solon, Ohio or Norton Industrial Ceramics, Worchester, Mass.

++ 1-1/2" dia. Sapphrox balls, Alumina Ceramics, Benton, Arkansas.

+++AD-85 1-1/2 gal. jars, Coors Porcelain Co., Golden, Colo.

† Attritor Al-S, Union Process Co., Akron, Ohio.

†† Zirbeads, Zircoa, Inc., Solon, Ohio.

†††Mini-media, Coors Porcelain Co., Golden, Colo.

account for impurity additions to the NASICON powders. In general, the percentage of media added to the powder was less than about 0.4%. Subsequent to the milling operation, two percent by weight polyvinylbutyral[§], or polyethylene glycol^{§§} was added as a binder in either an acetone or methanol slurry respectively. These slurries were pan-dried and the resultant powders were deagglomerated (by ball-milling for one hour) and classified by screening through an 80 mesh nylon screen.

Gel-Processing

The essential features of this process were reported by C. Marcilly et. al. [24] and J. A. Pompa et. al. [25]. The process involves the mixing of soluble or dispersible metal oxide precursor in solution followed by pyrolyzation of organic constituents to form an amorphous matrix. High surface area powders of excellent homogeneity are the distinct advantages of this particular process. Raw materials utilized in this preparation method included NaNO_3^* , $\text{NH}_4\text{H}_2\text{PO}_4^*$, citric acid^{*}, ammonium-zirconium-carbonate (AZC)^{§§§}, and colloidal silica^{***}. The function of the citric acid to aid in the formation of the glassy matrix according to known art. [24]. NASICON powders were prepared by dispersing the insoluble silica in a solution containing the remaining components followed by gentle heating between 90°C and 120°C where an amorphous mass forms. These mixtures were then decomposed at 400°C in a CO_2 atmosphere. Residual carbon was removed by calcining the mixtures at 900°C in an O_2 atmosphere for four hours. The resultant agglomerated powders were milled using equipment and procedures outlined previously for the mechanical mixture process.

§ B-76 Monsanto, St. Louis, Mo.

§§ Carbowax 3350 or 20M, Union Carbide Corp., San Francisco, Calif.

* J. T. Baker Co., Phillipsburg, Penn.

§§§Magnesium Elecktron, Inc., Flemington, N.J.

***Aerosil 200V, Degussa Products, N.Y., N.Y.

Sample Preparation and Sintering

Preformed bar samples (50.8mm X 12.7mm X 0.6mm) and tubes (16mm OD X 200mm length) were prepared by isostatic compaction at pressures between 208 and 381 MPa. Binders and lubricants were removed from these parts by bisquing at temperatures between 750°C and 900°C for one to two hours. Sintering of these materials was accomplished in open air environments at temperatures between 1150°C and 1375°C for time periods ranging from 1/2 hour to 24 hours. Weight loss during sintering and linear shrinkage were evaluated for all samples by monitoring mass and dimensional changes.

Pressure sintering experiments using conventional hot-pressing and hot-isostatic pressing was conducted for selected materials and samples. Uniaxial hot-pressing studies were performed in graphite dies at temperatures between 1160°C and 1240°C and pressures around 34 MPa. Selected pre-sintered samples were further densified using HLP sintering in Argon at 1100°C and pressures of around 104 MPa.

Characterization of NASICON samples

Following sintering, numerous physical property measurements were made. Mass densities were obtained by an Archimedes method using isobutanol as the liquid medium. Axial ionic resistivities were measured using a two-probe A.C. method described elsewhere. [10] Mechanical strengths were obtained using four-point modulus of rupture measurements on bar samples or by diametral ring tests on tube sections. Microstructural features were catalogued using optical and scanning electron microscopy techniques.

The overall composition of selected powders and samples was determined via spectroscopy methods by two independent laboratories[#].

[#] Ford Chemical Laboratories, Salt Lake City, Utah
Coors Spectrochemical Laboratory, Golden, Colorado

Chemical inhomogeneities and the extent of decomposition of these materials were monitored by several methods: (1) Quantitative x-ray methods were developed to determine the amount of "free zirconia" present in the powders and sintered samples. In some instances, a "direct-line comparison" technique was utilized. [26] Better reliability was obtained using an "internal standard" method in which known amounts of monoclinic zirconia powder were added to unknown samples. [26] The integrated intensities of the (111) diffraction line for monoclinic ZrO_2 were obtained for both "unknown" powder samples and for powder samples having "known additions". These data were then correlated by regression analyses to determine the amount of free zirconia present in the unknown powder samples. (2) Free sodium and phosphorous were determined by wet chemistry and spectrophotometry respectively. A sodium specific-ion electrode and potentiometric methods were utilized to determine leachable sodium on samples which had been previously crushed and sieved through a 100 mesh screen. [27, 28] Soluble phosphorous was determined from identically prepared samples by complexing the phosphorous using a color complexing acid-phosphomolybdic acid, (i.e., $H_3P(Mo_3O_{10})_4 \cdot 29H_2O$). [29] A single-beam spectrophotometer^{##} was then used to determine the amount of phosphorous. "Known addition" methods coupled with regression analyses were also utilized in the determination of free sodium and phosphorous.

Results and Discussion

Physical Properties of NASICON Ceramics

Physical property results for NASICON ceramics prepared at different compositions and under a wide range of processing conditions are given in Table I. These results summarize our studies on this material over the past several years.

^{##} Baush and Lomb Spectronic-20, Baush and Lomb, Los Angeles, CA

Differences in density values were found to correlate closely with the activity of the powder. Finer-sized powders possessing high intrinsic surface area were able to achieve reasonable density levels (i.e., $\geq 3.18 \text{ g/cm}^3$) regardless of the method of sintering. In general, deagglomerated powders which were essentially all submicron in size gave the best density values. Comminution was considered an important processing step for the attainment of "high density" material. In particular, it was demonstrated that attrition-milled powders universally gave the best densification characteristics for conventional firing methods. Hot-pressing and hot-isostatic pressing of NASICON improved the observed density values in most cases.

Note that regardless of composition or processing method, the resistivities of these materials are essentially identical. Unlike the beta-aluminas, the attainment of low resistivity values was easily accomplished and appeared to be somewhat independent of the phase purity of the material. Most of the materials reported on in Table I were not monophase, but contained small quantities of free monoclinic zirconia. In some cases, resistivities of less than 10 ohm-cm (300°C) were observed from samples which contained in excess of approximately 10% crystalline ZrO_2 .

Except for a few isolated cases, the mechanical integrity of all samples (even HIP sintered materials) was poor. Exceptionally high strengths ($>200 \text{ MPa}$) were observed in hot-pressed materials on occasion, but these results have generally not been reproducible. The cause for these low strength values is not fully understood at the present time. The mechanical integrity may be intrinsic to NASICON itself, or due to the presence of free ZrO_2 , or a result of coarse microstructural defects in the material.

An examination of the microstructural features of NASICON demonstrates that this material crystallizes into cubical-type grains of less than about $10\mu\text{m}$ in size. A representative microstructure is shown in Figure 1. Larger grains faceted to cubic shape and were

TABLE I

Physical Properties of NASICON Ceramics

Composition, Raw Materials and Processing Method	Density (g/cm ³)	Resistivity (ohm-cm 300°C)	Strength (MPa)
1. x=2; Na ₃ PO ₄ ·12H ₂ O, ZrO ₂ , SiO ₂ , MM, WBM, CS.	3.21 ± .02	4.2 ± .4	77 ± 19
2. x=2; Na ₃ PO ₄ ·12H ₂ O, ZrO ₂ , SiO ₂ ; MM, WBM, HP.	3.34	3.2 ± 0.2	212 ± 19*
3. x=2; Na ₃ PO ₄ ·12H ₂ O, ZrO ₂ , SiO ₂ ; MM, WBM, HIP.	3.27 ± .01	4.3 ± .2	56 ± 13
4. x=2; NH ₄ H ₂ PO ₄ , NaNO ₃ , AZC, SiO ₂ ; GP, DBM, CS.	3.10 ± .02	2.8 ± .5	66 ± 10
5. x=2.4; NH ₄ H ₂ PO ₄ , Na ₂ CO ₃ , ZrO ₂ , SiO ₂ ; MM, DBM, CS.	3.15 ± .01	2.9 ± .2	79 ± 19
6. x=2.4; NH ₄ H ₂ PO ₄ , Na ₂ CO ₃ , ZrO ₂ , SiO ₂ ; MM, AM, CS.	3.20 ± .01	3.7 ± .2	99 ± 14
7. x=2.4; NH ₄ H ₂ PO ₄ , Na ₂ CO ₃ , ZrO ₂ , SiO ₂ ; MM, AM, HP.	3.25 ± .00	4.0	90 ± 10
8. x=2.4; NH ₄ H ₂ PO ₄ , NaNO ₃ , AZC, SiO ₂ ; GP, DBM, CS.	3.03 ± .01	5.6 ± .5	36 ± 16
9. x=2.4; NH ₄ H ₂ PO ₄ , NaNO ₃ , AZC, SiO ₂ ; GP, AM, CS.	3.19 ± .00	2.9 ± .1	104 ± 77
10. x=2.4; NH ₄ H ₂ PO ₄ , NaNO ₃ , AZC, SiO ₂ ; GP, AM, HP.	3.26 ± .00	3.3	85 ± 30

MM - Mechanical Mixture

WBM - Wet - Ball Milled in either Acetone or Methanol

CS - Conventional Sinter

HP - Hot-Pressed

HIP - Hot-Isostatically Pressed

GP - Gel-Process

DBM - Dry-ball Milled

AM - Attrition Milled in Methanol

* Atypical strength - Although strengths as high as 282 MPa were observed for some hot-pressed samples, repeated measurements on identically prepared material averaged around 100 MPa.

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GEL PROCESS, $X=2.3$
POLISHED SURFACE

FIGURE 1

generally accompanied by coarse inter-granular pores. Thus the absence of any long-range contiguous structure and non-equilibrium grain boundaries accompanying these "square" grains may be a contributing factor to the observed low strength.

Another plausible reason for the observed low strength values may be attributable to the zirconia second phase. It is well documented that pure ZrO_2 exhibits a disruptive reversible phase transformation from monoclinic to tetragonal forms in the temperature range of 800°C to 1200°C. The presence of this second phase and its resultant transformation following densification could set up microcracks in the NASICON body resulting in low mechanical integrity. Such an occurrence has been qualitatively observed and is shown in the SEM photograph of Figure 2. Note that in several of the cubical NASICON grains, microcracks are clearly evident. Defects such as these would undoubtedly lead to poor mechanical strength.

The third major defect apparent in NASICON ceramics was the appearance of large semi-spherical voids. A typical void structure for a NASICON sample fired at 1375°C for 16 hours is shown in Figure 3. The initiation and growth of these spheres coincided with the decomposition of the material. Hot-pressed or HIP sintered samples were free of these gross defects and yet still gave poor strength characteristics. Any one or a combination of the foregoing microstructural defects may be the cause of the observed poor strength values in NASICON. However, whether or not NASICON is intrinsically weak, or whether the ZrO_2 second phase or flaws in the microstructure are directly responsible for the lower strengths remains to be resolved.

NASICON Densification Characteristics

Sintering studies have been conducted using both mechanical mixture and gel-process powders. The densification characteristics of these materials vary both with respect to composition and processing. In Figure 4 are shown the isothermal densification characteristics of a mechanically-mixed NASICON powder at a composition of $x=2$. Results

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FIGURE 2
NASICON GRAIN STRUCTURE SHOWING
MICROCRACKS IN MANY OF THE CUBICAL
GRAINS

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FIGURE 3
NASICON MICROSTRUCTURE SHOWING
THE PRESENCE OF LARGE SPHERICAL
VOID DEFECTS

LINEAR SHRINKAGE VS. SINTERING
TIME AT VARIOUS TEMPERATURES

FIGURE 4

such as these demonstrate that NASICON can be sintered to near theoretical density (+98%) in time periods as low as two hours at a temperature of $\sim 1260^{\circ}\text{C}$. Slightly lower temperatures markedly reduce the rate of the densification process. Approximately 16 hours are required to reach equivalent densities at temperatures around 1230°C . Note though that at higher sintering temperatures (i.e., 1260°C), bloating of the ceramic occurs for sintering times in excess of two hours. This particular phenomena coincided with the appearance of the semi-spherical voids in the ceramic as discussed earlier. An examination of the phase composition of these isothermally sintered samples indicated that expulsion of increasing amounts of ZrO_2 occurred concurrently with higher firing temperatures. This observation led us to postulate that NASICON melts incongruently. Quantitative x-ray analyses later demonstrated that such was the case. As shown in Table II the only crystalline phase present in samples sintered above 1310°C was ZrO_2 . The remaining constituents had apparently formed an amorphous glass.

Powders prepared by gel-processing methods were also characterized with respect to their densification behavior and phase composition for various sintering temperatures. Shown in Table III are the sintered physical property results of powders prepared at compositions of $x=2$ and $x=2.3$. Prior to firing these powders were essentially single-phase NASICON with only trace amounts of free ZrO_2 detectable by x-ray methods. However, the existence of single phase NASICON appeared to be highly dependent upon the selected composition and firing conditions. The presence of ZrO_2 as a second phase was clearly evident at all temperatures about 1175°C for the $x=2$ composition. In the $x=2.3$ composition, its appearance was not apparent until the temperature exceeded about 1250°C . Below this temperature, it was undetectable by x-ray methods. Density values for these samples followed the same trends that were presented earlier for the mechanical-mixture powders. Densities first increased with increasing firing temperature, then later decreased as copious amounts of ZrO_2 were

Table II

Phase Composition (by X-ray) of Sintered NASICON
Prepared from Mixtures of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, ZrO_2 and SiO_2

<u>Temp °C</u>	<u>Weight % NASICON</u>	<u>Weight % ZrO_2</u>
1150	97.8*	2.2*
1170	98.6	1.4
1185	97.7	2.3
1200	97.2	2.8
1215	96.4	3.6
1230	96.3	3.7
1245	94.6	5.4
1260	89.3	10.7
1275	77.2	22.8
1310	0**	45.6**

* This sample was the calcined powder lot. The remainder of the data is for sintered bar samples.

**At this temperature, the sample had completely melted. The only discernable phase present was ZrO_2 . The remaining material, (i.e. Na_2O , P_2O_5 , and SiO_2), had apparently formed a glass.

Table III

Properties of NASICON Ceramics Prepared from Gel-Process Precursor Powders

Sintering Conditions		Na ₃ Zr ₂ Si ₂ P _{0.7} O ₁₂ Composition			Na _{3.3} Zr ₂ Si _{2.3} P _{0.7} O ₁₂ Composition		
Time (hrs.)	Temp. (°C)	Density ($\frac{g}{cm^3}$)	Phase Comp.*	Strength MPa	Density ($\frac{g}{cm^3}$)	Phase Comp.*	Strength MPa
16	1175	3.10 ± .02	trace ZrO ₂	66 ± 10	2.45 ± .05	No ZrO ₂	42 ± 6
16	1200	3.12 ± .00	0.9% ZrO ₂	63 ± 8	2.73 ± .01	No ZrO ₂	55 ± 7
16	1225	3.11 ± .00	3.6% ZrO ₂	57 ± 11	2.81 ± .02	No ZrO ₂	52 ± 10
16	1250	3.16 ± .00	5.4% ZrO ₂	82 ± 0	2.97 ± .01	No. ZrO ₂	67 ± 4
16	1275	2.97 ± .01	10.2% ZrO ₂	38 ± 7	3.15 ± .01	0.9% ZrO ₂	73 ± 4
4	1300	Samples of this composition melt at these temperatures			3.15 ± .00	4.4% ZrO ₂	81 ± 10
16	1300	Samples of this composition melt at these temperatures			3.14 ± .01	7.0 ZrO ₂	67 ± 11

* The phase composition of these samples war apparently 100% NASICON except where noted.

expelled from the NASICON structure concurrent with the appearance of the large semi-spherical voids. Note that the melting of NASICON is apparently composition dependent. Compositions containing less phosphorous (but more soda and silica) melt at higher temperatures. Nevertheless, the general features of incongruent melting are apparent at all compositions. This work confirmed the earlier results obtained using mechanical mixture powders and therefore suggests that the decomposition of this material is independent of composition and processing methods.

Quantitative Characterization of NASICON Decomposition

In order to further evaluate the mechanics and characteristics of the decomposition of NASICON ceramics, one particular lot of gel-process powder was selected for study. The initial composition of this powder and samples fired over a range of temperatures spanning from 1150°C to 1375°C was determined using emission spectrography. Physical properties and the extent of decomposition were then quantitatively evaluated.

Table IV presents results from the emission spectrographic analyses for samples prepared and fired at various temperatures. Although some disagreement exists between the results obtained from the two laboratories, in general there appears to be little overall composition change related to changes in firing conditions. If anything, a slight decrease in the amount of phosphorous is observed at all conditions. Such a result is predictable given the volatile nature of phosphours.

Physical property data for samples sintered at various temperatures are presented in Table V. Again, trends observed earlier for mechanical mixture and gel-process powders of different compositions are also evident with this powder. However, due to the slightly different composition, optimum physical properties are obtained at a firing temperature of 1300°C. Note that the physical properties deteriorate rapidly in the temperature range between 1300°C and 1375°C.

Table IV

Bulk Composition of NASICON Samples
Fired at Various Temperatures*

Firing Condition	% P_2O_5	% SiO_2	% Na_2O	% ZrO_2
1. Calcined Powder- 900°C - 16 hours				
LAB A	7.7 ± .0	26.6 ± .1	19.7 ± .0	45.6 ± .0
LAB B	4.3 ± .9	26.1 ± .2	19.5 ± .8	50.1 ± .4
2. 1150°C - 16				
LAB A	7.5 ± .1	26.8 ± .1	19.5 ± .1	45.7 ± .1
LAB B	4.9 ± 1.3	27.7 ± .4	18.0 ± 1.8	49.0 ± 1.8
3. 1225°C - 16 hours				
LAB A	7.6 ± .1	26.7 ± .1	29.5 ± .1	45.8 ± .1
LAB B	5.1 ± .5	27.5 ± .6	19.6 ± .1	47.7 ± 1.1
4. 1300°C - 16 hours				
LAB A	7.7 ± .0	26.7 ± .1	19.7 ± .0	45.7 ± .2
LAB B	5.4 ± .6	26.5 ± 1.8	19.8 ± 1.3	48.2 ± 3.3
5. 1375°C - 16 hours				
LAB A	7.7 ± .1	26.6 ± .1	19.7 ± .1	45.7 ± .2
LAB B	5.1 ± .5	27.8 ± .3	19.5 ± .8	47.3 ± 1.3
6. Cumulative Values				
LAB A	7.7 ± .1	26.6 ± .1	19.7 ± .1	45.7 ± .2
LAB B	5.1 ± .5	27.8 ± .3	19.5 ± .8	47.3 ± 1.3
7. Formulated Amounts	7.91	26.77	19.56	45.76

* Quantitative Emission Spectrography on Three Replicate Samples of each Condition

LAB A - Ford Chemical Laboratories, SLC., UT

LAB B - Coors Spectrochemical Laboratory, Golden, CO

Table V

The Physical Properties of NACICON Ceramics as a Function
Sintering Temperature

Gel Process Powder Lot R21100

<u>Firing Condition</u>	<u>%Weight Loss</u>	<u>Density*</u>	<u>Resistivity**</u>	<u>Strength⁺</u>
1150°C--16 hours	.295 ± .018	2.64 ± .01	3.7 ± .1	72 ± 1
1225°C--16 hours	.280 ± .049	3.15 ± .00	2.8 ± .1	91 ± 15
1300°C--16 hours	.521 ± .064	3.19 ± .00	2.9 ± .1	104 ± 77
1375°C--16 hours	1.566 ± .137	2.92 ± .01	8.9 ± .0	8 ± 4

* Expressed in g/cm³

** Expressed in ohm-cm (300°C measurement)

+ Four-point bend measurement on bar samples in MPa.

Significant melting of the material was not observed until the temperature exceeded 1375°C.

In-house analyses of these samples were developed and conducted to determine the extent of decomposition. In doing so, it was postulated that the NASICON structure itself would be fairly insoluble in water whereas constituents such as free Na_2O and P_2O_5 would be easily solubilized and therefore subsequently analyzed by wet-chemistry techniques. Free ZrO_2 was monitored using quantitative x-ray methods. Decomposition of the material was therefore evaluated as a function of firing conditions by determining the extent to which these three constituents were excluded from the NASICON structure. Listed in Table VI are the quantitative results of this work. These data demonstrate that all three constituents are exsolved from the NASICON structure as a consequence of higher firing temperatures. Note especially that a minimum in the amount of each constituent was obtained at the 1225°C firing temperature. It is believed that at this temperature, the material has optimally reacted. Higher temperatures result in a reversal of this reaction process eventually ending up with a completely disassociated and liquified body. Microstructural characterization of these samples indicated that the initiation of the void structure shown in Figure 3 actually begins at around the 1225°C firing temperature. Higher firing temperatures simply result in void enlargement.

Several of the samples sintered in accordance with conditions shown in Table IV were exposed to constant humidity environments for periods up to 225 hours. All samples showed significant weight gain and exhibited needle-like crystal growth on exposed surfaces. Samples fired at higher temperatures displayed more weight gain and extensive crystal growth. Shown in Figure 5 is a SEM photograph depicting one such crystal on the surface of a NASICON sample. An EDAX analysis of this particular crystal indicated it to be a sodium phosphate (Na_3PO_4). Confirmation of this observation was later obtained by performing x-ray diffraction analyses on a number of crystals scrapped from sample surfaces. Additionally, Auger microprobe analyses of similar samples indicated that higher

Table VI

Compositional Analysis of NASICON ceramics as a
Function of Sintering Temperature

Firing Conditions	Weight % ¹ Free Na ₂ O	Weight % ² Free P ₂ O ₅	Weight % ³ Free ZrO ₂
1150°C - 16 hours	2.10 ± .12	.51 ± .05	4.69 ± .30
1225°C - 16 hours	1.64 ± .10	.37 ± .04	2.90 ± .14
1300°C - 16 hours	1.99 ± .06	.60 ± .02	3.41 ± .43
1375°C - 16 hours	2.40 ± .15	.92 ± .03	8.32 ± .21

¹ Determined as Na⁺ using a specific -ion probe.

² Determined as an orthophosphate using spectrophotometry.

³ Determined as monoclinic crystalline ZrO₂ using x-ray methods.

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FIGURE 5
 Na_3PO_4 CRYSTAL GROWTH FROM
THE SURFACE OF A NASICON
CERAMIC ELECTROLYTE

concentrations of phosphorous were apparent on fracture surfaces (inter-granular fracture) than within the bulk.

The foregoing data and observations clearly demonstrate the temperature sensitive nature of this material. Of peculiar interest is the fact that the densification (i.e., shrinkage) and decomposition apparently occur simultaneously. Whereas most crystalline ceramic materials exhibit densification at 0.6 to 0.8 times their respective melting points, NASICON ceramics achieve densification at temperatures greater than or equal to 0.9 times their melting point. Although the exact nature of the densification and decomposition mechanics are not understood, it appears that the decomposition of this material provides the driving force for densification. In other words, in the temperature range where decomposition occurs, the diffusivities of constituent elements are enhanced. The shrinkage rate is therefore increased due to these enhanced diffusivities. Densification probably occurs due to the deposition of the decomposition product at neck areas between adjacent grains. Thus decomposition of the material lowers the bulk free energy while shrinkage minimizes surface energy resulting in a net reduction in the total free energy of the system. This is diametrically opposed to "reactive sintering" where phase homogenization enhances the driving force for densification. Apparently, in NASICON ceramics, dissociation gives rise to enhanced sintering. In this sense, it can almost be classified as "reverse-reaction sintering". Unfortunately, the shrinkage process is short lived. Densification appears to lead to sealing of pores and the entrapment of gaseous product (such as a P_2O_5 , Na_2O or a combination of these constituents). As the temperature is raised, the decomposition pressure is increased, and large spherical voids ensue. Bloating of the ceramic is therefore observed. Overall, such a process leads to a multiphase inhomogeneous product containing coarse microstructural defects.

Clearly, much additional work remains in the development of NASICON ceramics. Significant processing problems have yet to be overcome before strong, conductive, and durable NASICON ceramics can be produced

using conventional processing methods. In particular, alternative compositions, or additives to the ceramic should be investigated in an effort to prepare bodies which do not undergo decomposition during densification.

Summary and Conclusions

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 non-uniform 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.

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