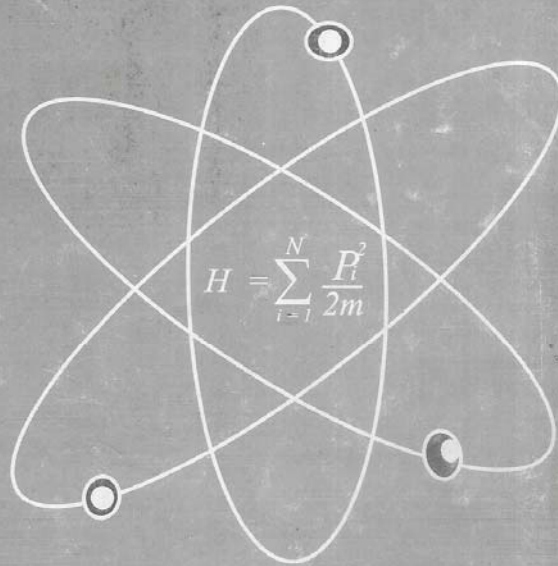


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SINTERING CHARACTERISTICS AND ENERGY APPLICATIONS OF SODIUM SUPERIONIC CONDUCTORS (NASICONs): A REVIEW

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ABSTRACT

Ionic conductors are increasingly playing a crucial role in today's electronic devices from electrochromic displays, lithium ion batteries for laptop computers and mobile phones to gas sensors for detection of environmental pollutants, among others. Traditional materials exhibiting good ionic conductivity have been Na-beta alumina-based cells or those made from Li(Co, Ni)O₂. However, these materials and others that were subsequently produced have some defects in terms of their stability in operation, when used in energy storage devices, their conductivity and structure, 2-D or 1-D, layered, etc., all impact on their overall performance. Thus the search for new materials led to the synthesis of NASICONs which have better ionic conductivity comparable to beta-alumina attributed to their 3-D structures suitable for easy diffusion of ions, and substitutionability by other ions of the same size or less, like lithium, in their flexible structures. Moreover, they can be synthesized at much lower temperatures. This explains some of the attraction for the research in these materials. However, there are still problems with the solid state synthesis of these materials which include the phase purity challenge, grain boundaries, among others, which are the subject of this review. Several methods are being developed to improve or eliminate these defects through novel sintering techniques such as SPS and PLD, for improved sintering properties and thin-film deposition techniques for NASICONs, respectively. Also alternative materials are being researched that are easier to synthesize relative to NASICONs-the so-called NASICON analogues.

Keywords: NASICON, Superionic conductor, sintering and ionic conductivity

1.1 INTRODUCTION

NASICON is short for **Na-Super-Ionic-CON**ductor. It is an inorganic ionic conducting material that exhibits high ionic conductivity by Na⁺ ions and is basically ceramic and polycrystalline. It belongs to a family of materials known as Superionic conductors (SICs). Superionic conductors come in various varieties: crystalline, non-crystalline, polymer, rubbery or glassy in nature and share the characteristic of high ionic conductivity at elevated temperatures[1]. At room temperatures they are insulators and their conductivity is of the order of 0.0001-0.1Ω⁻¹cm⁻¹(300K). Typical examples are AgI, RbAg₄I₅ and β-alumina, M₂O.xAl₂O₃, where M = Li, Na, Ag, K, Rb, NH₄, etc. Many inorganic Superionic conductors have been studied based on their ionic conducting properties, such as Ag₂SO₄ and Li₂SO₄ and their solid solutions [1]. Superionic conductors where the conductivity, σ_i is more than 0.1 Ω⁻¹cm⁻¹(300K) and activation energy for ion transport E_i is small(about 0.1.eV) are called Advanced Superionic conductors(AdSIC). The famous example in this category is RbAg₄I₅, where the conductivity is >0.25 Ω⁻¹cm⁻¹ at 300K and electronic conductivity is negligible.

Their conductivity is due to the existence of voids, vacancies in the system, which enables the ions to move freely. The mobile ions may be cationic or anionic and are generally, Li^+ , Na^+ , K^+ , Ag^+ , Rb^+ , etc., which are cationic. However, they may also be anionic, such as O^{2-} and F^- . There is a strong correlation between the ionic conductivity and the structure of the compounds, as the ions are massive and have size to move through the crystal structure.

Superionic conductors are also referred to as Solid Electrolytes (SE) or Fast Ion Conductors (FICs) due to their use as solid state energy storage systems, such as rechargeable lithium ion batteries, Solid Oxide fuel cells, etc. At zero Kelvin they are perfect insulators and the lattice is almost perfect with zero defects (vacancies). However, at non zero temperatures the thermal energy is enough to create some defects in the crystal, through which the ions can move. The defect type may be Schottky or Frenkel. In the Frenkel defect an ion moves from its lattice site to an interstitial site and leaves its site vacant. Another neighbouring atom can easily move into the site and leave its own site vacant, resulting in ionic conduction and so on. This is known as vacancy mechanism and is thought to be the conduction mechanism in NaCl. Similarly, the atom that moves into the interstitial site may move within the interstices and thus contribute to ionic conduction. This is called interstitial mechanism. A final mechanism known as interstitialcy mechanism involves the cooperative motion of one or more ions, from lattice site to interstitial, thereby displacing some atoms in their way. This is thought to be the conduction mechanism in Na- β alumina. These microscopic motions can be determined by Quasi-elastic neutron scattering (QENS) or NMR technique. The former can determine the microscopic ion dynamics, spatiotemporally, while the latter can give information about the spatial distribution of the ions which can lead to a determination of the nature of the conduction mechanisms in these materials.

Recent developments tend to focus on developing new materials for specific applications or to enhance the existing ones by changing or re-engineering the structural parameters by synthesis, using different routes (solid state, hydrothermal and sol-gel) or by change of the composition of the compounds for the applications in view: energy, medical, nuclear waste disposal, etc. The problems reported here are based on the solid state synthesis. There is need to characterize these materials to ascertain their structures and their relationship with physical properties, such as electrical, thermal and phase, among others, in order to suit the application in view.

Sodium Superionic conductor (Na^+), NASICON has attracted scientific and technological attention for about 40 years. This has been largely due to their potential applications in energy related or environmental concerns. NASICON which was first reported in 1976 has a general formula $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$; $0 < x < 3$. The highest conductivity is obtained for monoclinic structure for $x \sim 2$ [2, 3]. They have been proposed as solid electrolytes for applications in ion selective electrodes and sodium Sulphur batteries, Khireddin et al, [4]. The original composition of NASICONs were solid solutions derived from $\text{NaZr}_2\text{P}_3\text{O}_{12}$, by partial replacement of P by Si with sodium excess (to balance the negative charges) to generate the general formula earlier mentioned.

In this review the emphasis has been on solid state synthesis of these materials, usually in polycrystalline form, the problems and challenges faced by researchers in their synthesis and the various methods that have been adopted or proposed for the resolution of most of these problems. The research is based on the current work being carried out by the authors on Sodium Zirconium Phosphate, NZP of stoichiometry, $\text{Na}_{1-x}\text{Li}_x\text{Zr}_2(\text{PO}_4)_3$, $x=0-1$ ($x=0.0, 0.25, 0.50, 0.75$ and 1.00) using solid

state and hydrothermal methods. Attention has been paid to the problems faced in the practical application of these materials in devices, the ultimate goal, and in particular, electrochemical devices, including the various attempts that have been made to develop new materials (NASICON analogues or types) that have simpler structures and are easier to synthesize yet at the same time present less challenge in their application. Similarly, the structural features of these materials have been discussed due to the strong dependence of their physical properties on composition and crystallographic parameters and to their relevance in the optimal performance of these materials.

As the World increasingly demands miniaturization of electronic devices, NASICON research has also focused on novel techniques for producing nanocrystalline and thin film NASICONs, as conventional deposition techniques are inadequate and problematic for these materials. The objective of the work is to bring to the fore the nature of research taking place in this field so that the problems would be on the research agendas of solid State Physicists, Materials scientists and Engineers, in particular, on the research and challenges in the science of these materials given their relevance and how they can be implemented in our context, where materials and materials characterization facilities, if available, other bottlenecks could blunt the sharp minds of even the most optimistic and dogged researcher's ability to carry out full characterization of the materials for meaningful research.

2.1 GENERAL STRUCTURAL FEATURES AND PARAMETERS

Sodium Zirconium Phosphate, $\text{NaZr}_2(\text{PO}_4)_3$ (NZP) is a good representative of this family of compounds and would be used to elucidate the special features of these materials. The crystal structure consists of a strongly bonded but flexible three-dimensional network of PO_4 tetrahedra and ZrO_6 octahedra. The polyhedra are interconnected through corner sharing and develop a rigid and highly stable hexagonal lattice with structural holes that are partially or fully, depending on the composition, occupied by Calcium, Strontium, Sodium or any other substituting ions [4].

The mobile ions partly occupy a three-dimensionally linked interstitial space. Hong [2] has observed that the smallest cross-sectional areas of an interstitial passageway, called "bottlenecks", should have the same diameters greater than twice the sum of the anions and mobile alkali ion radii[5]. The compound has two symmetries: in the range $1.8 \leq x \leq 2.2$ the material is monoclinic with space group $\text{C}2/c$; the rest of x yields a rhombohedral unit cell of the $\text{R}\bar{3}c$ space group at room temperature.

It has been observed that at higher temperatures ($\sim 200^\circ\text{C}$), the NASICON takes the rhombohedral symmetry in the entire x range. Phase transition involving Na^+ sublattice occurs at this point. The geometrical features of the skeleton and its interstitial space satisfy the criteria for fast ion Na^+ transport. The Superionic transition at 200°C is accompanied by an almost equal Na^+ distribution over the available sites, being only partially occupied. XRD studies of monoclinic $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$ have revealed large isotropic thermal scattering factor for Na^+ indicating a weak localization of the ions and evidence of increased conductivity due to structural features.

XRD measurements are free to move whereas those in dilatometric measurements are constrained. As a result microcracking has been observed during cooling from the sintered state in such materials through the detection of their acoustic emission as a result of thermal strain they undergo, Srikanth [4].

4.1 THERMAL PROPERTIES OF NASICONs

Sintering is a method of making objects from powder by heating them below their melting points, until their particles adhere to each other, that is they form bonds and this has traditionally been applied for manufacturing (synthesizing) ceramic materials. The materials are heated at high temperatures for different lengths of time, starting with calcinations to remove volatiles at temperatures up to 600°C. The objective, in the case of NASICON is to heat (fire) them at high temperatures, 1200-1500°C, to bring about fusion of the particles of the constituent compounds. This is very important as it reduces the porosity of the material, a necessary requirement for electrical characterization in terms of impedance analysis of the samples, and is usually accompanied by phase transitions. The phase changes, transition temperatures, weight losses, structural changes and other microstructural features that occur in the materials are often revealed by a combination of DSC(differential scanning calorimetry) or DTA(differential thermal analysis) thermogravimetric analyses(TGA), XRD, scanning electron microscopy(SEM) and dilatometric measurements, among others.

High sinter density and good mechanical strength are desired characteristics for enhancing the utility of these materials. The preparation or synthesis of these materials must be tuned to the performance and desired objectives, e.g. for electrical properties. Several efforts have been made to improve these properties: the use of grain growth inhibitors such as $Zr_2P_2O_9$ and by the use of some fine particles in some family of compounds. There have also been attempts to alter the axial thermal expansion coefficients by proper ionic substitution and these have helped in overcoming some of the problems to a great extent [4].

An advantage of NASICON materials over other materials used as solid electrolytes is their low sintering temperature, compared to, say, Na- β -alumina. They exhibit crystalline forms, depending on their temperature and composition. One of the most challenging problems with sintered NASICON is the presence of certain amount of ZrO_2 second phase[8] and a monoclinic to tetrahedral phase transition that occurs at 1100°C, below the usual sintering temperature of the NASICON.

Another monoclinic to rhombohedral transition of crystalline NASICON around 200°C causes a dilatometric anomaly unfavourable for applications. A way of overcoming such problems through compositional modifications has been reported by Van Alphen, H.Kholer, S.Fugitsu et al[9]. The van Alphen NASICON has the general formula $Na_{1+x}Zr_{2-x/3}Si_xP_{3-x}O_{12-2x/3}$ and contains little ZrO_2 second phase.

Kang and Cho [9] have carried out a systematic study of such compositions and tried to correlate the crystalline NASICON, the phase formation, sintering behavior and electrical conductivity of the compounds with synthesis technique, which has rarely been reported. They compared the properties of the Alphen- and Hong-type NASICON, for two representative compositions: $Na_3Zr_2Si_2PO_{12}$ and $Na_{3.2}Zr_{1.3}Si_{2.2}P_{0.8}O_{10.5}$. The result showed that it is essential to choose an appropriate sintering temperature and cooling rate to produce sintered NASICON with less ZrO_2 and high electrical conductivity.

5.1

The poor sinterability and phase purity limits the applications of NASICONs in practical devices. A fundamental problem faced in solid state synthesis of these materials at high temperatures is the volatilization of Na_2O and P_2O_5 and the resultant segregation of Zirconia at the grain boundary. This has been known to be responsible for the decrease in ionic conductivity, Ahmed et al [9]. Some methods that have been implemented to improve the situation include sol-gel synthesis, yttria doping and Spark Plasma Sintering (SPS) technique, among others; of these SPS needs some elaboration. The technique, reported by Lee et al [9] uses microscopic electrical discharges between the particles under pressure and thus allows quick densification to almost the theoretical density. These enhancements have been observed in several metallic, ceramic and other systems. It also has an advantage of a relatively lower temperature and minimal grain growth and has been applied to fabricate nanostructured materials [9].

NASICON presents significant challenge to solid state Physicists, material scientists, inorganic chemists and materials engineers, in terms of understanding of its complex structure (which may contain up to 100 atoms per unit cell); the lack of single crystals-most materials are polycrystalline-as the art of producing single crystals is yet to be perfected coupled with their attendant problems and the non stoichiometric nature of its compositions. These various problems are being studied by various groups.

One alternative that is being pursued is to develop new Superionic conductors with simple structures, the so-called NASICON analogues which are easier to synthesize. Superionic phosphates and silicates are in this group. A member of the group which has been reported recently [10] and which have been synthesized by the hydrothermal technique, is Potassium Iron (III) pyrophosphate (KFeP_2O_7). Also on the basis of its good ionic conductivity and low cost, rhombohedral $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ -a NASICON-type, is seen as a potential insertion electrode material in lithium polymer batteries. The rhombohedral phase is found to be unstable and when heated above 579°C , it turns into monoclinic modification [11]. Although the phase remains stable upon cooling to room temperature, monoclinic $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ exhibits several reversible phase transitions with temperature, Anderson et al [11].

5.1 NASICONs AND ELECTROCHEMICAL APPLICATIONS

These materials (NASICONs) were initially suggested as electrolytes to replace the conventional Na- β -alumina batteries. However, it was later discovered that NASICON-based cells are not stable when in contact with molten (Na) sodium electrodes. Nonetheless, possible application of NASICON in Na, K or Co,Fe sensors have already been demonstrated. Indeed NASICON based CO_2 sensor has already been proposed [10].

Na-S batteries have also been regarded as one of the potential candidates for such applications due to their high energy storage and power, compared to other battery systems, however, the requirement that the electrolyte must have high resistivity against degradation while in operation and requirement of high mechanical strength, among others, limits their use [9]. Na- β -alumina would have been applied in the Na-S battery but it has a 2-D layer structure which makes it exhibit anisotropic characteristics in thermal expansion and electrical conductivity, causing mechanical failure of the cell after operation for some few hours [8]. However, the NASICON, $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_2\text{O}_{12}$, is found to be stable in molten sodium and can be obtained at 1200°C , which is a great advantage, compared to above 1500°C for the preparation

of Na- β -alumina [5]. The conductivity in NASICON is only slightly lower than that in Na- β -alumina as both compounds have the highest known alkali conductivity at room temperature.

6.1 NASICON THIN- AND NANOCRYSTALLINE-FILMS

Solid materials with high ionic diffusivity are of vital interest in materials science due to their potential applications as solid electrolytes. Thus one of the aims in materials science is to understand the physical principles determining the transport properties of solids so that new materials can be designed with tailored diffusion features. The diffusion features of a given polycrystalline ionic conductor can be changed by reducing its grain size down to the nanometre range; this is equivalent to increasing the volume fraction of interfacial regions and introducing a large number of grain boundaries. The transport properties of these regions may however deviate considerably from those of the bulk, thus the procedure may have remarkable impact on the ionic diffusivity of the material. Many a time grain boundaries in nanocrystalline materials provide fast diffusion pathways for small cations and anions like Li^+ and F^- or even larger anions like O^{2-} leading to an enhancement of the diffusivity, Bork and Heitjans [12]. Sometimes however, the interfacial regions have a blocking effect thus reducing the ionic conductivity.

Until recently, all electrochemical devices using Superionic conductors have been made from either bulk material or thick films ($>0.1\text{mm}$). In order to obtain high current densities it is necessary to produce thin components, this reduces the resistance. In some applications, oxygen sensors for example, integration of the devices requires the sensing materials to be in the form of thin films. Unfortunately, there is difficulty in producing such thin films by conventional techniques due to the inherent problem of maintaining exact stoichiometry. Production of NASICON thin films had always been an objective. Conventional thin film methods like sputtering, for example, leads to a significant loss of some volatile elements such as Na and P from NASICON thin film due to their composition-dependent conductivity. Good control of film stoichiometry is very important in these substances. Pulsed Laser Deposition (PLD), technique has been used by different groups, and has been applied successfully to deposit thin films. This is due to the advantage in PLD to transfer the correct stoichiometry. The fundamental objective in such pursuit is to produce NASICON ceramic films that are thin, dense, contain extremely fine crystalline grains (nanocrystalline) and are primarily ionic conductors.

There are unresolved challenges in this area however, such as the excessive number of grain boundaries in the nanocrystals; how to restrain grain growth during the high temperature densification process so that the crystallites can remain nanosized after processing and the daunting task of maintaining the chemical and physical stability of these films.

7.1 CONCLUSION

NASICONs are very interesting and challenging materials to synthesize characterize and study. The importance and potential applications of these materials are diverse if the present problems can be overcome and justifies the persistence in the study of these materials. Apart from electrochemical devices, NASICONs have potential applications in the fields of nuclear waste disposal, the use of NZP, bio-materials, ion selective membranes and sensors. The problem of producing single crystals with well formed features and appropriate size continue to interest researchers as new techniques continue to evolve for improvement. High temperature solid state reaction continues to dominate the production of these substances, though hydrothermal synthesis is increasingly being utilized for its low

temperature route. The issue of reducing grain growth and sinterability is a challenge which researchers continue to face in the PLD technique, the production of thin films and nanocrystalline components appropriate for the miniaturization of electronic devices are being pursued.

Some of the facilities needed include the full features of scanning electron microscopy (SEM) machines, thermal analyzer systems (DTA, DSC, TGA), XRD machines with capacity for determination of relevant crystallographic parameters and elemental characterization facilities such as XRF, AAS and EDS, among others. The use of neutron activation analysis (NAA) technique has recently been reported [13] using the Nigeria Research Reactor-1(NIRR-1) for elemental characterization. This is a rarely reported method for the analysis of these materials and will be used in this research to correlate with the conventional methods mentioned above.

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