GROWTH AND CHARACTERIZATION OF SOME NEW SUPERIONIC PHOSPHATES

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A B S T R A C T

The search for new sodium superionic conductors is becoming very popular with the development of NASICON whose ionic conductivity is equivalent to that of Na β - alumina. NASICON poses a challenge to Materials Scientists in understanding its structure and conduction mechanism due to the lack of single crystals, non-stoichiometry in the composition, zirconium deficiency, etc. It is a solid solution between $NaZr_2P_3O_{12} - Na_4Zr_2Si_3O_{12}$. Then came several new triorthophosphates, which became popular as NASICON analogues with their simple structures and stoichiometric composition. However, all the compounds whether NASICON or NASICON analogues always had only the triorthophosphate end members and their structures were directly related to $Na_3Sc_2P_3O_{12}$. Here, the author reports the ionic conductivity in condensed phosphates, particularly pyrophosphates, for the first time, showing high ionic conductivity. These pyrophosphates have been grown by hydrothermal method. The author has reported some of these pyrophosphates in brief as the perspective superionics very recently. These condensed phosphates are much easier to obtain in the form of single crystals with stoichiometric composition. The structures vary from the regular NASICON type. Although, cations form the usual octahedra, Na^+ atoms lying in the cavities, but the framework linking differs. The conductivity is attributed to the diffusion of Na^+ through a network of tunnels in a rigid structure made up of pyrophosphate anions sharing corners with ZrO_6 / MO_6 octahedra. This has opened a new chapter in the search for new Na^+ superionic conductors even among the condensed phosphates and silicates. The pyrophosphates considered here have a wide range of cationic groups. The author has discussed in the present work, the growth, structure and impedance spectroscopy of these new pyrophosphate superionics.

1. INTRODUCTION

In recent years, there has been a continuous search for new superionic conductors for various device applications like high temperature solidstate batteries, fuel cells, specific ion and gas sensors, electro-chromic displays, ion-exchanged membranes and so on. The superionic conductors exhibit ionic conductivities comparable to those of molten salts of liquid electrolytes while still being in solid phase. These materials include the following types:

> Fast ionic conductors
> Fast proton conductors
> Fast anionic conductors

There is no precise definition for superionic materials so far. According to Suresh Chandra[1], a superionic solid should show the following characteristics:

1. ionic bonding
2. high electrical conductivity (10^{-4} to 10^{-1} $Ohm^{-1} Cm^{-1}$)
3. principal charge carriers are ions
4. very low electronic conductivity
5. low activation energy (of the order 0.1 eV to 1.0 eV)

Ionic conductivity in solids was first reported by Faraday.[2] Subsequently Warburg[3] described the migration of Na^{+} ions through glass and its precipitation on the surface of glass when a direct current flowed through the glass. Nernst[4] reported in 1899, high ionic conductivity in mixed oxides at high temperature. In 1914 Tubandt and Lawrence[5] detected the extraordinary high silver conductivity of the α - phase of AgI which exists above 147° C. Its conductivity ranges between 1.2 and 2.6 $(\Omega\ Cm)^{-1}$ which is comparable to the best conducting liquid electrolytes.

Subsequently a lot of other superionic conductors showing uni-dimensional, two-dimensional, and three-dimensional ionic conductivity were reported. Some of the most famous superionics are Na/β - alumina, Na/β'' - alumina, titanates, boracites, silicates, phospho-silicates, phosphates (NASICON and its analogues), sulphates, etc. NASICON became the most popular superionic conductor with a three-dimensional ionic

conductivity in contrast to the Na β'' - alumina and all other earlier reported superionics which exhibited one or two - dimensional ionic conductivity.[6] But today, NASICON poses a challenge to solidstate physicists with reference to its structure, stoichiometry, synthesis, zirconia deficiency, conduction mechanism and a host of other problems.[7]

The study of Na^+ ion conductors has become very popular, particularly after the development of the NASICON group of superionic conductors. In fact, NASICON ($Na_{1+x} Zr_2 Si_x P_{3-x} O_{12}$; $0 < x < 3$) is a solid solution in the system $NaZr_2P_3O_{12}$ - $Na_4Zr_2Si_3O_{12}$ and is being studied extensively by a large group of workers throughout the world, because of its applications as a solid electrolyte in high temperature Na/S batteries.[2] The high ionic conductivity, which is higher than Na β - and Na β'' - alumina is mainly due to the high mobility of Na^+ ions through tunnels in a rigid structure of PO_4/SiO_4 tetrahedra sharing corners with ZrO_2/MeO_6 octahedra. Many variations have been investigated by appropriate substitutions in the NASICON system. The basic structure of most of these derivatives remains that of $Na_3Sc_2P_3O_{12}$. NASICON has two structure types viz. NASICON and anti-NASICON. When Hong[8] reported the structure of NASICON for the first time (fig.1), only one site for Na^+ was proposed. Recently Boilet et al[10] have identified five different structural sites for Na^+ , out of these only Na_1^+ is mobile. Therefore, the material scientists continue to strive to develop new superionic conductors with simple structures, and phosphates are found to be the most suitable ones.

II. SUPERIONIC PHOSPHATES

The study of superionic behaviour in phosphates is at least one decade old. Some of the phosphates, particularly condensed phosphates were reported as superionic conductors on par with silicates.[11-13]

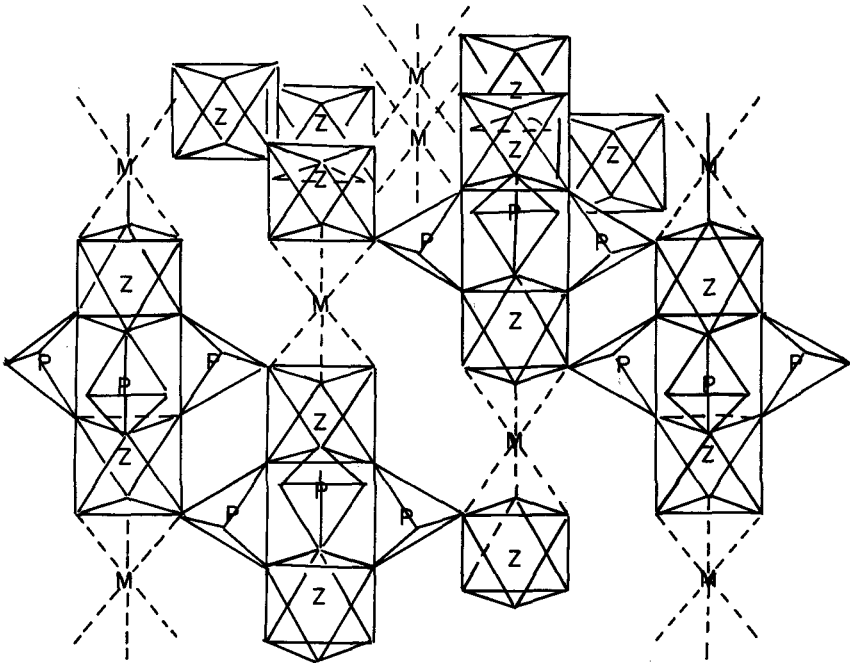The ionic conductivity in these phosphates is only in the order of 10^{-5} to
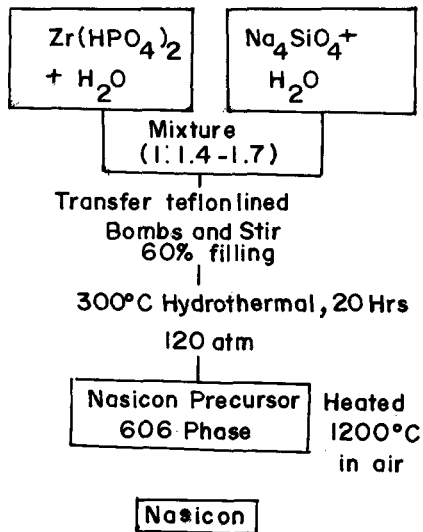
Fig.1. Structure of NASICON.[8]

Fig.2. Flow diagram showing the hydrothermal procedure to develop NASICON.[21]

10^{-7} $(\text{r}\ Cm)^{-1}$. The interest in the development of pure superionic phosphates appeared only recently, when there was a search for new Na^+ superionic conductors they become popular as NASICON analogues. The structures of these phosphates consist of a three dimensional framework of atoms. Based on these a series of new NASICON analogues like $Na_3M^{+2}(PO_4)_3$, $M = Sr, Mg, Fe, Mn$ [14] ; $Na_2(R, M^{+3})M^{+4}(PO_4)_3$ [15]; $A_3M_2^{+3}(PO_4)_3$, $A = Li, Na, Ag, K; M = Cr, Fe$ [16,17], etc. were synthesized only with an intention to develop simple compounds with stoichiometric composition and relatively simple structures. However, all these new compounds did contain only the ortho-group of radicals irrespective of a wide variety of them. In fact, it was found that these structures are directly related to the basic NASICON structure reported by Hong.[8] The author has recently reported for the first time pyrophosphates showing high ionic conductivity. Hitherto none of the phosphates having condensed radicals and showing a high ionic conductivity has not been reported. The crystal chemical characteristics of these new superionic phosphates will be discussed later.

III. CRYSTAL GROWTH

In general the NASICON group of ionic crystals are being obtained by two techniques like flux growth and solid state reactions. Melt technique has not been attempted not only because, of the higher melting points, but also due to the multiple phase transitions. As it was earlier stated that NASICON is a solid solution in the system $NaZr_2P_3O_{12}$ - $Na_4Zr_2Si_3O_{12}$, this has resulted in the synthesis of only twinned crystals. The single crystal growth has not been attempted by these two techniques, and this led to the lack of data on the conduction mechanism. Although, several refinement techniques were adopted on NASICON, the results varied from one group to another. Also they found the existence of zirconium deficiency associated with the presence of condensed radicals like $[P_2O_7]$, $[P_3O_9]$, $[Si_3O_8]$, etc. in the final products. If one can overcome all these problems, it would be easy to understand NASICON clearly. Hence, in the last few years there is a strong move to look for other Na^+ superionics. The group led by the author has successfully

obtained a new series of Na^+ superionics belonging to NASICON family, but the
pure end members of phosphates. The group has obtained crystals of $Na_2(R,M^{+3})M^{+4}P_3O_{12}$
where $M^{+3} =$ Al,Fe,Cr,Bi; R = rare earths, $M^{+4} =$ Zr,Ti and a group of pyrophosphates,
by various techniques like solid phase synthesis, flux growth and hydrothermal tech-
nique. The latter to be the most suitable not only to grow crystals but also to un-
derstand the phase equilibria within the given system, which is highly essential to
develop a growth technology for any compound. Unfortunately the literature available
on the growth of superionics, particularly belonging to NASICON family is highly
limited and only a few scanty reports and in some cases only a hydrothermal proces-
sing of the materials obtained by solid state reactions are adopted.[21,22] For exam-
ple, the authors[21] have adopted the hydrothermal procedure to develop NASICON and
it is shown in the form of a flow chart (fig.2). It was found that by hydrothermal
method NASICON indicates that insufficient silicon is incorporated into the resul-
tant products. Also these authors indicated that it is possible to develop a stoi-
chiometric NASICON compound through hydrothermal reactions. The problem only arises
when silicon is added into the system. Keeping this as a prelude, the present author
has obtained pure phosphate phases by hydrothermal technique which helped in several
ways. The presence of condensed radicals like $[P_2O_7]$, $[P_3O_9]$, $[P_4O_{12}]$ and $[P_5O_{14}]$ in the
in the pure triorthophosphates could be avoided, because these condensed radicals
normally form the bottle necks for the conducting media. Similarly the formations
of twinning was reduced and it is permitted in many cases to obtain pure single cry-
stals of a particular phase. Here the author discusses in brief the development of
the hydrothermal growth of phosphates having condensed radicals. The synthesis of
phosphates by hydrothermal method in general started during 1950s. Both rare earth
orthophosphates and aluminium-orthophosphates were obtained at this time. The higher
volatility of the P_2O_5 creates a major problem in the synthesis of rare earth phos-
phates under hydrothermal conditions. The formation of orthophosphates from HCl solu-
tions at $105 - 300^o$ C and at a pressure of 90 atms has been described by earlier

workers.[23] Monocrystals of Monozite $CePO_4$ were synthesized from aqueous solutions of 85 % H_3PO_4 at 300° C using teflon liners.[24] The $GdPO_4$ crystals were obtained using aqueous solutions of HCl and $NH_4H_2PO_4$ at temperature 150 - 160°C and pressure 1.5 kbars.[25] Similarly Berlinite, $AlPO_4$ was obtained.[26,27] However, the first systematic attempt to grow condensed phosphates under hydrothermal conditions was made by Yoshimura et al.[28] In general the hydrothermal technique is quite complicated, particularly for the growth of phosphates. This may be due to the following reasons:

1. Lack of growth technology
2. High volatility of phosphorus at higher temperature
3. High reaction susceptibility of phosphorus
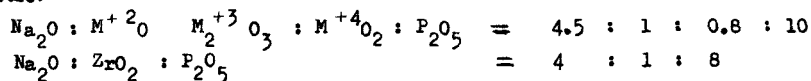4. Corrosive nature of phosphorus at higher temperature

Of course, one can overcome all these problems through a systematic and careful study of phosphates using the modern instrumentation technique. High volatility of phosphates can be controlled using a special outlet to the crystallization chamber. The other important problem that phosphorus corrodes even the metals like Pt, Ir, Nb, Au and Ni can be solved by replacing them by vitreous carbon glass and teflon liners. The main drawback in using the vitreous carbon glass liners is sealing. If one can seal these vitreous carbon glass liners by some means, the growth of pure phosphates can be carried out even at higher temperature by hydrothermal method.

In the present work the author reports the hydrothermal growth of some super-ionic phosphates, particularly the pyrophosphates $Na_2MZr(P_2O_7)_2$, (M = Ni,Co) and $(Na_{0.66}Zr_{0.33})P_2O_7$.

The synthesis of phosphates by hydrothermal technique normally results in the crystallization of orthophosphate, because of the higher P_2O_5 and H_2O pressures. It has been earlier studied in detail with reference to the crystallization of condensed radicals by hydrothermal techniques which insists normally lower water vapour pressure.[28-30] The author[31] has made some conclusions based on the water vapour pressure to explain the possible reasons for the absence of the condensed phosphates
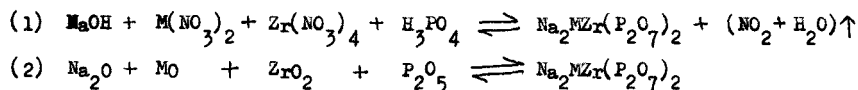
in nature. Keeping this in mind the author has carried out the present hydrothermal synthesis experiments at relatively low pressure and temperature i.e. at 220° C and 50 to 60 atms. The alkaline component was taken in the form of a solution (NaOH) with a known molarity and this solution acts as a mineraliser. The starting materials such as the oxides of zirconium and the desired transitional metal were taken in required amounts in a teflon liner, later 85 % H_3PO_4 was poured into it. The superionic phosphates under consideration were obtained under the following molar ratio:

$$Na_2O : M^{+2}O \quad M_2^{+3}O_3 : M^{+4}O_2 : P_2O_5 \quad = \quad 4.5 : 1 : 0.8 : 10$$
$$Na_2O : ZrO_2 : P_2O_5 \quad = \quad 4 : 1 : 8$$

The growth of pyrophosphate crystals was carried out in Morey type autoclaves (length 15 cm, internal diameter 3.5 cm) with teflon liners of capacity 25 ml. The cross section of the autoclave used in the synthesis is shown in fig.3. The crystallization was carried out by spontaneous nucleation which was controlled by a systematic rate of heating. The starting materials such as $M^{+4}O_2$ was taken in the required amount in a teflon liner. The liner was filled with 85 % H_3PO_4 . The alkaline component (Na$_2$O) was taken in the form of a solution (NaOH) with a known molarity and this solution acts as a mineralizer. The author could synthesize pyrophosphate superionics under the following conditions: temperature 250° C, pressure 150 atms, mineralizer 1.5 M NaOH.

In the growth of double pyrophosphate superionics, the addition of surplus P_2O_5 did not change the resultant product which can be explained from the influence of H_2O vapour pressure in the system. Surplus P_2O_5 should actually result in the formation of simple or compound orthophosphates. But owing to the lower water vapour pressure maintained within the system, the reproducibility of pyrophosphates could be achieved. The following reactions would explain the synthesis of the present compounds:
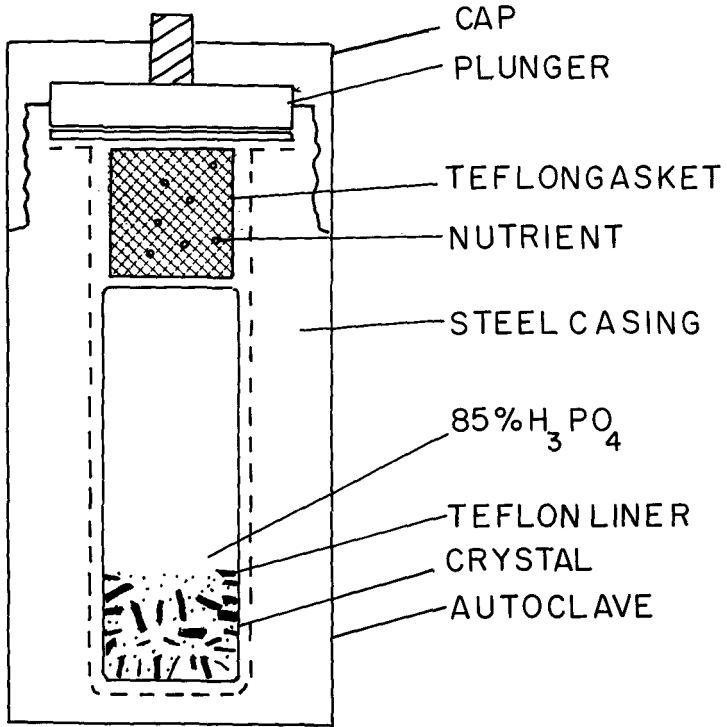
(1) $NaOH + M(NO_3)_2 + Zr(NO_3)_4 + H_3PO_4 \rightleftharpoons Na_2MZr(P_2O_7)_2 + (NO_2 + H_2O)\uparrow$

(2) $Na_2O + MO + ZrO_2 + P_2O_5 \rightleftharpoons Na_2MZr(P_2O_7)_2$

Fig.3. Hydrothermal apparatus.

The crystals obtained were superior in size from 0.5 to 2 mm. Twinning was almost absent and crystals have well developed morphology with vitreous lustre. The characteristic photographs of these crystals are shown in figs.4a,b,c. In the growth of pyrophosphates $(Na_{0.66} Zr_{0.33})_2 P_2 O_7$ the experiments were carried out exactly under similar conditions as in the previous case. However, the difference is in the ratio of the starting materials and the type of trivalent metals added into the nutrient. Both Bi and Ce were added into the nutrient in the form of oxides and nitrates respectively in relatively larger quantity. But surprisingly both Bi and Ce have not entered into the composition of this pyrophosphates. This has led to think about role of cations in the crystallization of these superionic phosphates. The results are in good agreement with the earlier reports that the divalent metals enter easily into the structure than except a few trivalent metals.[14] Hence, in the present work phosphates containing divalent metals like Ni, Co, Mn, Cu have been obtained in the form of well developed single crystals with perfect morphology. The authors have carried out a large number of experiments using trivalent metals like lanthanides, transitional metals like Cr,Fe,Bi,Al,Co. But it was found that only Al enters the composition more easily than other trivalent metals. Similarly the lanthanides, inspite of surplus concentration, did not enter the composition and therefore, only a limited number of superionic phosphates containing trivalent metals were obtained. The best ones are $Na_2(R,Al)ZrP_3O_{12}$: R = La,Ce,Nd. The presence or absence of rare earth was confirmed through ICP and XRF. Even in the earlier report where $Na_3M_2(PO_4)_3$ M = Sc,Cr,Fe was obtained,[16] the crystals were not of good quality and showed multiple phase transitions, which varied among Sc - Cr - Fe. This is mainly connected with the framework structure of these phosphates. The important aspect of this report is the growth of condensed phosphates by hydrothermal technique at relatively lower temperature. In the earlier reports, the growth of RP_5O_{14}[28,29] and $MNdP_4O_{12}$[30] was carried out at elevated temperatures in order to get rid off the possibilities of the entry of OH^- molecules in the grown crystals. Further
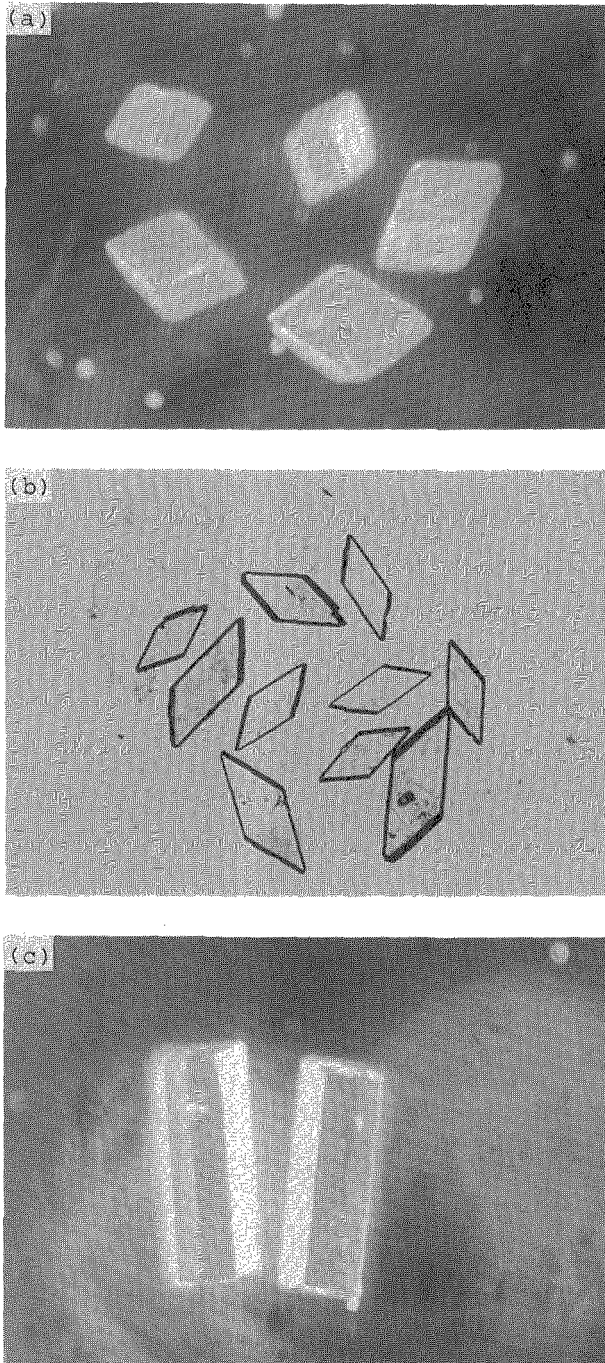
Fig.4. Characteristic photographs of $Na_2CoZr(P_2O_7)_2$ crystals.

the size of the RP_5O_{14} crystals obtained by hydrothermal technique was only 0.1 to 0.3 mm at 650° C.[28] Here the author reports the growth of very well developed crystals with a size of 1 - 4 mm at relatively very low temperature. Thus concluding the role of cations and volatiles like P_2O_5 and H_2O in the crystallization of these superionic phosphates. The study of infrared spectra of these phosphates showed the absence of mixed radicals in the resultant products. This is the most important pre-requisite for any superionic compound. The addition of trivalent metal into the nutrient yielded several metastable phases also in the final products. Thus the hydrothermal growth of superionic phosphates has greater scope in order to obtain good single crystals which in turn helped to understand the conduction mechanism.

The hydrothermal growth elucidation of mixed double pyrophosphates has been carried out in greater detail, particularly with reference to the cobalt bearing pyrophosphates. The morphology of $Na_2CoZr(P_2O_7)_2$ depends mainly upon the concentration of P_2O_5 in the system. The fig.5 shows the schematic diagram, how the morphology varies with the concentration of P_2O_5 . It is clearly observed that the prism faces dominate over the pyramidal faces as the P_2O_5 concentration increases. Similarly, an attempt has been made to study the growth rate of $Na_2CoZr(P_2O_7)_2$ crystals against the concentration of P_2O_5 and H_2O fig.6. These figures show a critical point beyond which the growth rate falls sharply. This helps to fix the optimum conditions for the growth of $Na_2CoZr(P_2O_7)_2$. In order to study the growth rate and other morphological features a good and well developed spontaneously grown crystal was used as a seed which was kept at the bottom of the autoclave. Although, the growth elucidation for $Na_2CoZr(P_2O_7)_2$ is given in brief, it emphasises the importance of such studies for the successful growth of any superionic phosphate in general. However, a further detailed research is highly essential to understand the growth technology for these superionic phosphates.
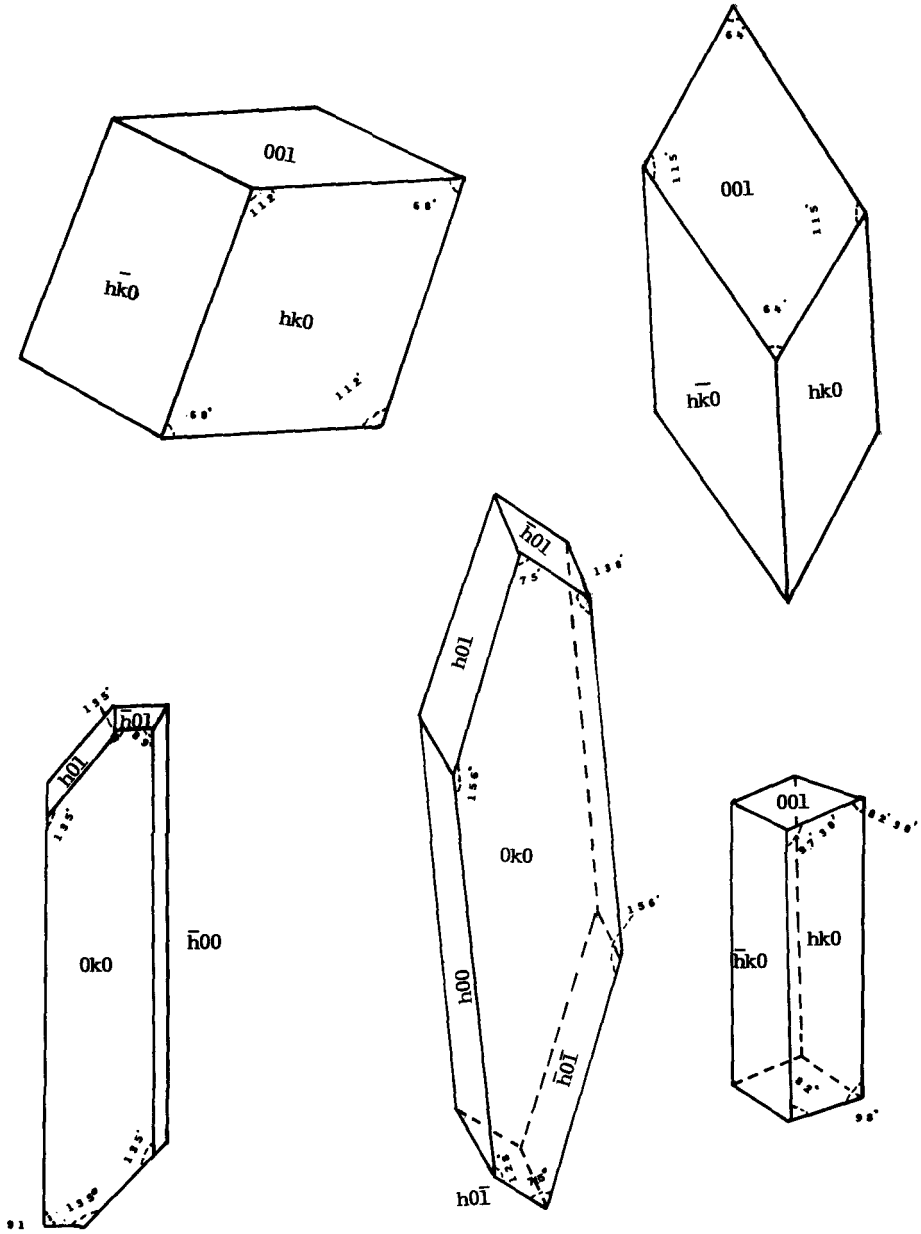
Fig.5. Schematic diagram showing morphological variation of
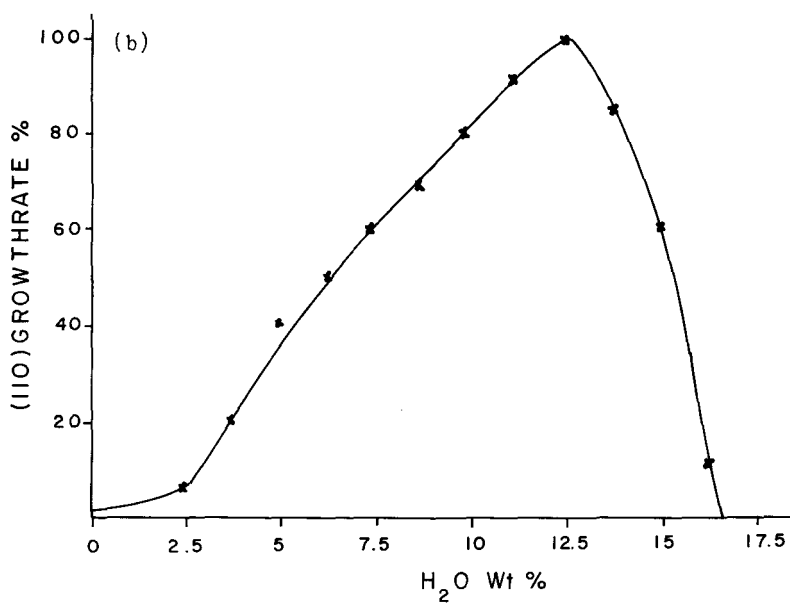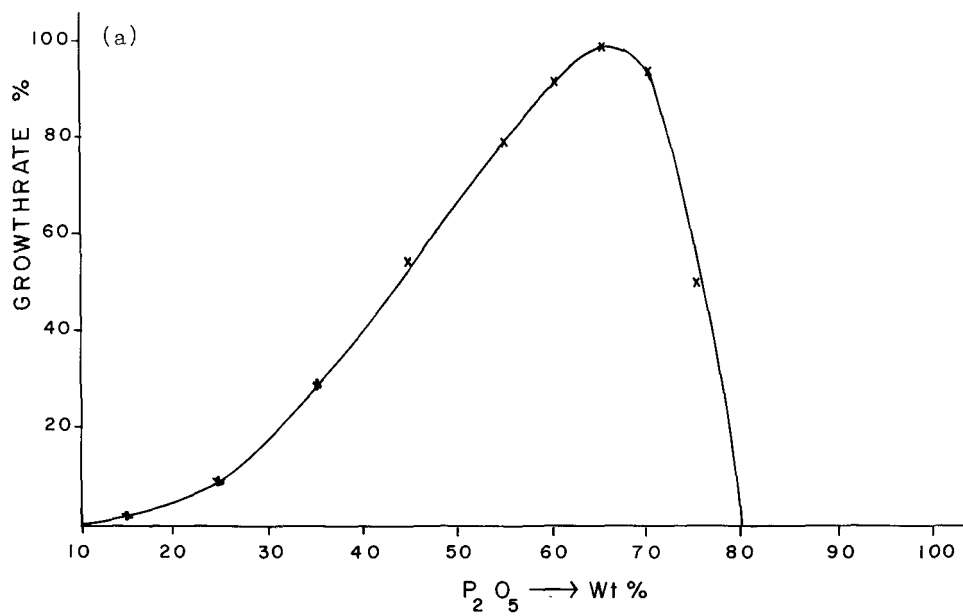$Na_2CoZr(P_2O_7)_2$ with P_2O_5 concentration.

Fig.6. Dependence of the growth rate of $Na_2CoZr(P_2O_7)_2$ crystals against the concentration of P_2O_5 (a) and H_2O (b).

IV. CHARACTERIZATION

IV.a) Crystal Structure: The crystal structure of NASICON and some NASICON analogues are given earlier in section 1. The crystal structure of these compounds and bond types directly control the single crystal growth of these superionic phosphates and the possible cationic entry into the final composition and also the application or superionic behaviour. Hence, the study of crystal structure is an important aspect in the growth and characterization of superionics. With this aim a single crystal structural refinement work has been carried out for some of the representative compounds in each group:

$$Na_2MZR(P_2O_7)_2 \qquad M = Co,Ni$$

$$(Na_{0.66} Zr_{0.33})_2 P_2O_7$$
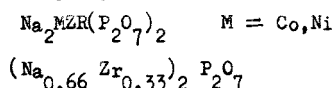
Although, the cations form usual octahedra and Na atoms lying in the cavities but framework linking differs in each type. The cell parameters for these compounds are given in table 1.

In the structure of $Na_2MZr(P_2O_7)_2$, two different dipyrophosphate anions connect Zr distorted octahedra signallizing the main bond chains of the framework. Each Zr atom situated conventionally in the origin sharing an edge with the second octahedron in the structure occupied by Ni or Co. Two independent Na^+ atoms are located in irregular polyhedra. The projection of the structure of $Na_2NiZr(P_2O_7)_2$ is given in fig.7. Close examination shows that two independent Na^+ atoms are located in irregular polyhedra and most apparent diffusion path of Na to be along (001) direction. Average distances of both Na(1) – O = 2.628 Å, and Na(2) – O = 2.564 Å are comparable to the values reported in other Na ionic conductors.

In the structure of $(Na_{0.66} Zr_{0.33})_2P_2O_7$, Na^+ and Zr atoms are located in the same general position surrounded by a distorted octahedra in each diphosphate Oxygen atoms. The PO_4 tetrahedra in each diphosphate anion are related by a binary axis possessing through the oxygen atom linking both P – atoms. Diphosphate anions are arranged in a sort of trigonal packing slices parallel to (001) with thickness

TABLE 1. Cell parameters of some superionic pyrophosphates

Compound	Crystal system	Space group	Axial lengths, Å			Axial angles, $^{\circ}$			V, gcm^{-3}
			a	b	c	α	β	γ	
$Na_2NiZr(P_2O_7)_2$	Triclinic	P1	6.461(3)	7.257(4)	6.501(3)	123.24	91.95	93.79	253.5(1)
$Na_2CoZr(P_2O_7)_2$	Triclinic	P1	6.535(3)	7.266(4)	6.496(3)	122.96	92.28	93.75	257.2(1)
$(Na_{.66}Zr_{.33})_2P_2O_7$	Orthorhombic	–	6.867(5)	12.345(4)	27.527(5)	–	–	–	2333(2)
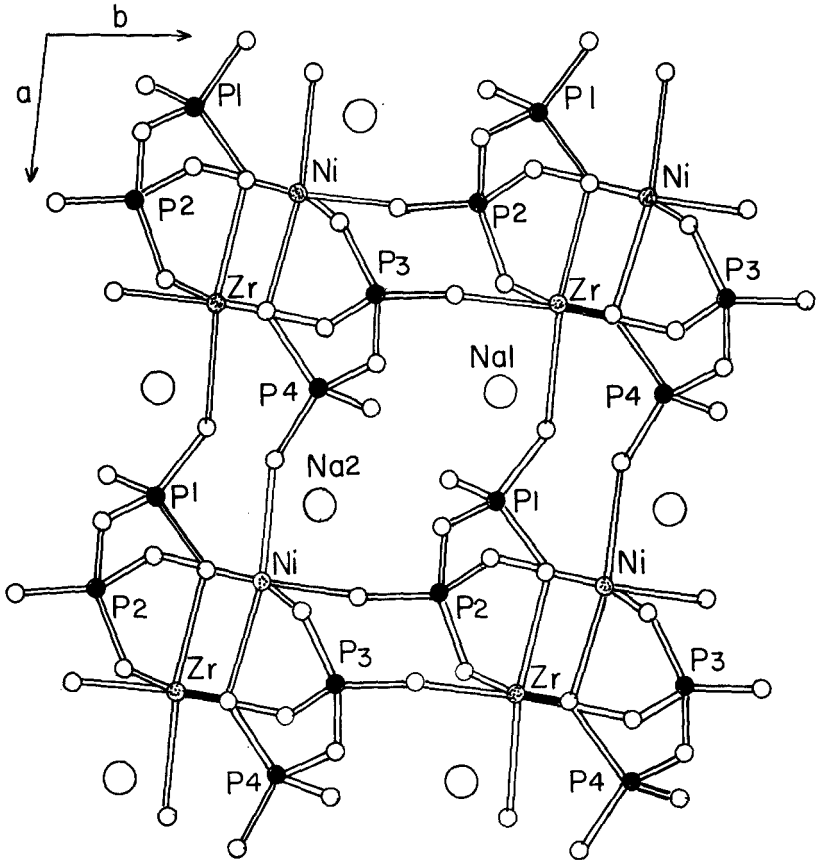
Fig.7. Projection of the structure of $Na_2NiZr(P_2O_7)_2$.
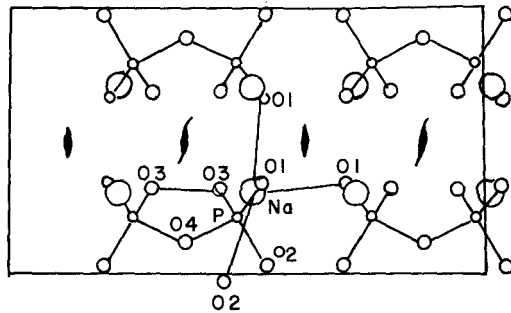

Fig.8. Projection of the structure of $(Na_{.66}Zr_{.33})_2P_2O_7$

C/8 . In these slices, (Na,Zr) octahedra from strips parallel to (110) by sharing edges which in turn connect different anions.

(Na + Zr) − O bonding distances are intermediate between typical Na − O distances in similar ionic conductors (2.6 $\mathring{A}$) and those encounter in ZrO_6 octahedra (2.15 $\mathring{A}$). The composition of the present compound is to be compared with the so called NASICON (sodium, zirconium, scandium phosphoro-silicates) ratio Na/(Zr,Sc) is 3/2, but in the present structure, Na^+ and Zr atoms are occupying the same crystallographic position. It is thought that Si could be introduced in this structure partially substituting for P, making this compound very similar in composition to non-stoichiometric NASICON described by Rudolf et al.[32] Indeed $(Na_{0.66}Zr_{0.33})_2$ P_2O_7 could be orthorhombic, structure type synthesized by the above authors as a precursor of the non-stoichiometric. Figure 8 shows a projection of the structure down the a-axis. The structure consists of a kind of trigonal arrangement of anions in slices parallel to (001) with thickness C/8. In each slice, the anions are linked together by chains of $(Na,Zr)O_6$ octahedra parallel to either (110) or (-110). Each octahedron is connected to five P_2O_7 anions and 3 of them in the slice through atoms O(1) and O(2). In consecutive slices related by Z fold axes, octahedra chains in directions (110) and (-110) share edges defining a distorted tetrahedron formed by O(1) atoms around the empty 8a Wyckoff position with symmetry 222 (fig.9). The blocks founded by 2 of such slices are connected through O(2) atoms.

Thus the above structural study shows clearly, even the condensed phosphates can go as superionic conductors and hence it has opened a new chapter in solid state science in the search for new superionic conductors even among condensed phosphates and silicates.

IV. b) Differential Thermal Analysis: Differential thermal analysis was carried out for representative samples using Stanton Redcroft apparatus with a temperature programmer. The internal standard used was pure Al_2O_3 powder. The DTA curves of $Na_2(La,Al)ZrP_3O_{12}$ and $Na_2M^{+2}Zr(P_2O_7)_2$ where M = Co,Ni, crystals exhibit phase
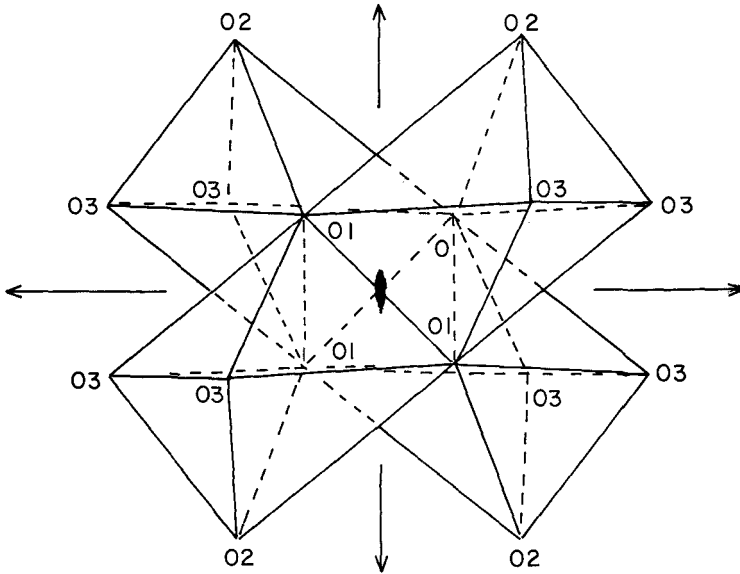
Fig.9. Octahedral chains in directions   110   and   -100
       share edges defining a distorted tetrahedron formed by
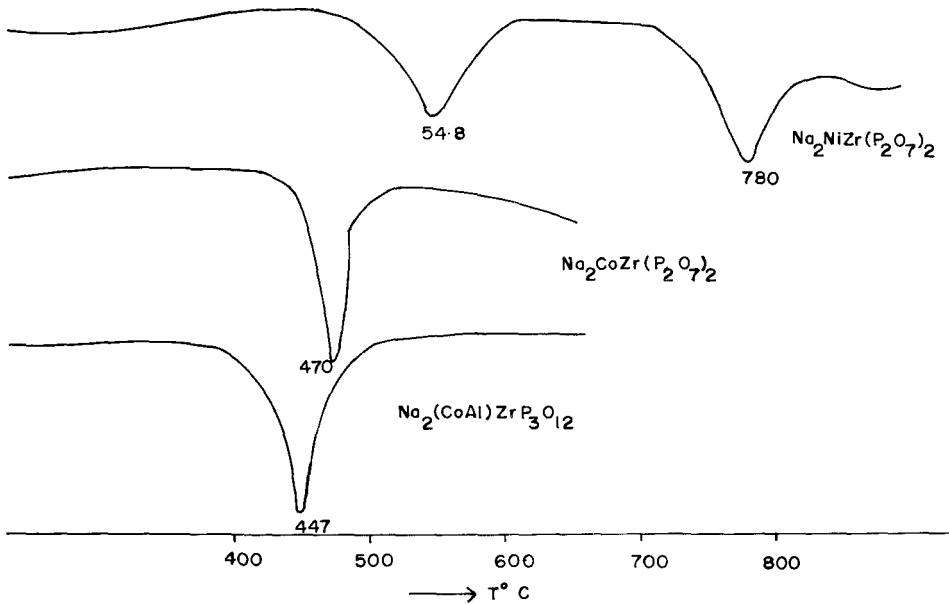   O(1) atoms around the empty 8a Wyckoff position with
       symmetry 222.
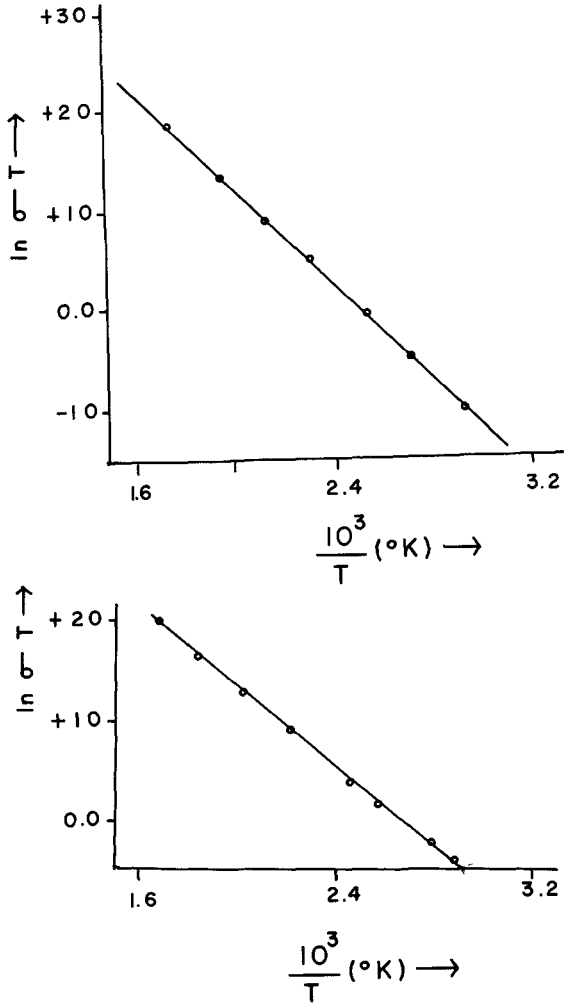

Fig.10. DTA curves for some representative superionics.

Fig.11. Arrhenius plots of ln σ T Vs. 10³/T .

transitions at various temperatures (fig.10).

$Na_2(La,Al)ZrP_3O_{12}$ and $Na_2CoZr(P_2O_7)_2$ have only one endothermic phase transition at $447^{\circ}C$ respectively. Whereas Ni bearing crystals show two endothermic phase transitions at 548° and 780° C. Hence, these materials are very good prospective superionic materials.

IV. c) Impedance Spectroscopy: The impedance measurements were carried out according to the technique adopted by earlier workers.[33] The crystals of pyrophosphates by applying 5 tn^{-2} pressures. The pellets (diameter 10 mm, thickness 3 mm, compactness 85 - 90 %) were provided with blocking silver electrodes on either side. The pellets were sintered in a vacuum chamber (10^{-2} torr) at 300° C. An impedance analyser (HP 4192A, USA) was used. The pellets were placed inside a cylinder which was evacuated (10^{-2} torr) and kept inside a tubular furnace (with a three terminal arrangement).

The ionic conductivity measurements were carried out from room temperature up to 300° C within a wide range of frequencies (dc to MHz). The Arrhenius plots of $\ln \sigma$ T against $10^3/T$ are shown in fig.11. The activation energy values were calculated and are given in the corresponding Arrhenius plots. The ionic conductivity values in general vary from 10^{-2} to 10^{-3} $(Ohm,Cm)^{-1}$ at about 300° C.

The values of ionic conductivity and the congenial structure of these pyrophosphates make them prospective superionic materials.

V. CONCLUSIONS

A high ionic conductivity in these new pyrophosphates and the congenial structures have led to the search for new soidum superionics not only among ortho-group of phosphates, but also among other condensed phosphates and even silicates, which together form a greater prospective to the field of superionics.

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