

## SYNTHESIS AND CHARACTERIZATION OF NEW SUPERIONIC TRIORTHOPHOSPHATES

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New superionic triorthophosphates,  $\text{Na}_2(\text{La}, \text{Me}^{3+})\text{M}^{4+}(\text{PO}_4)_3$  and  $\text{NaMe}_2^{2+}\text{M}^{4+}(\text{PO}_4)_3$  (where  $\text{Me}^{2+} = \text{Ni}, \text{Cu}, \text{Mn}$ ;  $\text{Me}^{3+} = \text{Co}, \text{Al}, \text{Cr}, \text{Fe}$ ;  $\text{M}^{4+} = \text{Ti}, \text{Zr}$ ), were synthesized by chemical reactions and the hydrothermal method. The advantages and disadvantages of each of the methods have been discussed with reference to morphology and some of the physical properties. The crystals were characterized by XRD, SEM, DTA and the measurements of ionic conductivity. The ionic conductivity values were found to be of the order of  $10^{-2}$  to  $10^{-1}$  ( $\text{ohm cm}^{-1}$ ) at  $300^\circ\text{C}$  and the activation energy values for ionic motion were in the range 0.16–1.0 eV.

### 1. Introduction

NASICON was the most popular material available for many years as the source material for high temperature battery devices, but for the past one or two years the interest has been slowly declining, because of some problems like the difficulties connected with the synthesis, lack of stoichiometry in the final products, lack of single crystals, zirconium deficiency and a host of other problems [1]. For example, when Hong [2] reported the structure of NASICON for the first time, only one site for Na was proposed. Quite recently, Collin et al. [3] have identified five different structural sites for Na. Hence, the structure of NASICON is highly complex. Owing to all these difficulties, materials scientists are trying to synthesize crystals having more simple structures, stoichiometric in composition and which are easy to synthesize in the form of single crystals. These materials are mostly pure phosphates and the structural analogues of NASICON, i.e.  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ , and have led to the development of a new class of superionic triorthophosphates. Since the crystallization temperature of these pure phosphates is below  $900^\circ\text{C}$  (chemical reactions) and around  $300^\circ\text{C}$  (hydrothermal reactions), research into these materials is popular. The authors [4–6]

have reported earlier the synthesis of some of these superionic triorthophosphates. In the present report the authors give the synthesis and characterization of new superionic triorthophosphates.

### 2. Synthesis

$\text{Na}_2(\text{La}, \text{Me}^{3+})\text{M}^{4+}(\text{PO}_4)_3$  and  $\text{NaMe}_2^{2+}\text{M}^{4+}(\text{PO}_4)_3$  crystals were synthesized by two methods: (i) chemical reactions and (ii) a hydrothermal method:

(i) Chemical reactions: this method is very popular for the synthesis of sodium superionic conductors in general. Although the method is simple, the results are not satisfactory, because there is little control over the synthesis except for variation in the temperature of synthesis and the molar ratio. The starting materials, such as  $\text{Na}_2\text{CO}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{ZrOCl}_2/\text{TiO}_2$ ,  $\text{Me}^{2+}\text{Cl}_2/\text{Me}^{3+}\text{O}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ , were taken in a definite molar proportion in a platinum crucible and fired at  $900^\circ\text{C}$  for 24–40 h followed by a slow cooling to room temperature. The resultant products were polycrystalline and always twinned. The size of the crystals was small and microscopic. The morphology was equidimensional to massive and the crystals were not suitable for single crystal studies. The authors have varied the temperature of synthesis, rate of heating/cooling and the molar ratio of the starting

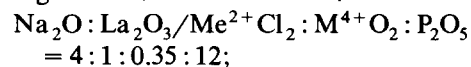
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components, in order to obtain good single crystals, but the results were not satisfactory. The only advantage of this method is its simplicity. Hence, the hydrothermal method has been preferred by several workers in the recent years.

(ii) Hydrothermal method: the synthesis of phosphates by hydrothermal method is quite complicated and it is recent [7,8]. The present authors have been advocating this method for many years [1,9], particularly for growing superionic triorthophosphates. An introduction of Si into the system (to obtain compounds belonging to the NASICON group by hydrothermal method) makes it highly complex and the synthesis becomes impossible at lower temperatures. The hydrothermal growth technology for pure phosphate end members itself is yet to be understood precisely.

The experiments were carried out in Morey type autoclaves (15 cm length, 3.5 cm internal diameter) using Teflon liners of capacity 25 ml. A

large number of experiments were carried out under varying conditions, i.e. within a temperature range of 200–300°C, pressure range of 100–250 atm, and a change in the molarity of the mineralizer solution. The alkaline component was taken in the form of molar solution with a definite molarity and this solution (NaOH solution) acts as a mineralizer. The starting materials, such as  $\text{La}_2\text{O}_3$ ,  $\text{Me}^{2+}\text{Cl}_2/\text{Me}^{3+}\text{O}_3$ ,  $\text{M}^{4+}\text{O}_2$  and 85%  $\text{H}_3\text{PO}_4$ , were taken in a Teflon liner. The authors could grow single crystals of  $\text{NaMe}_2^+\text{M}^{4+}(\text{PO}_4)_3$  and  $\text{Na}_2(\text{La}, \text{Me}^{3+})\text{M}^{4+}(\text{PO}_4)_3$  under the following conditions:



Temperature of crystallization = 250°C;

Pressure = 100 atm;

Mineralizer = 1.5M NaOH.

Since these compounds show a negative temperature coefficient of solubility under hydrothermal conditions, the furnace temperature was slowly

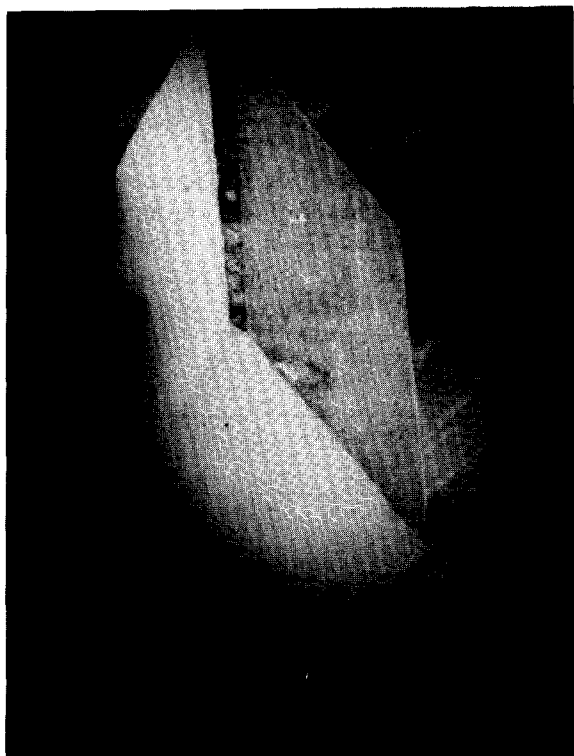


Fig. 1. A characteristic photograph of  $\text{Na}_2(\text{La}, \text{Co})\text{Zr}(\text{PO}_4)_3$  crystals.

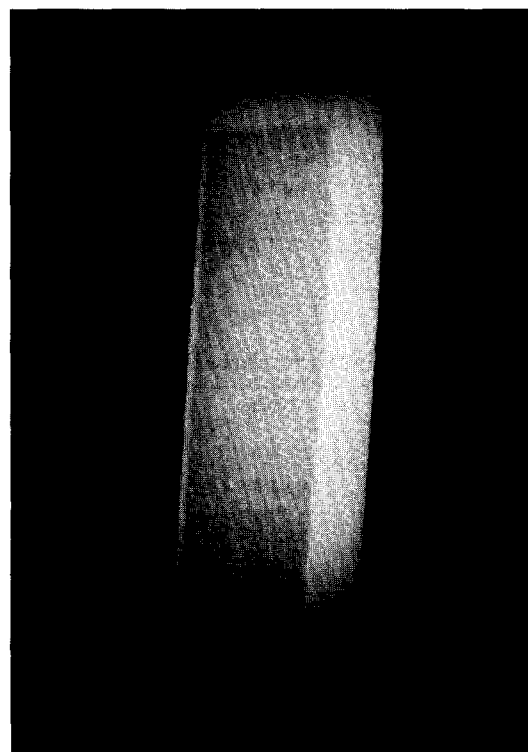


Fig. 2. A characteristic photograph of  $\text{NaNi}_2\text{Zr}(\text{PO}_4)_3$  crystals.

raised up to a predetermined point and held for 10 days. The crystals obtained by this method had an increased size and showed a well developed morphology with smooth surfaces (figs. 1 and 2). Twinning was almost absent and the properties of these crystals were superior when compared with those of crystals obtained by chemical reactions.

### 3. Results and discussions

$\text{Na}_2(\text{La}, \text{Me}^{3+})\text{M}^{4+}(\text{PO}_4)_3$  and  $\text{NaMe}_2^{2+}\text{M}^{4+}(\text{PO}_4)_3$  crystals were characterized through XRD, DTA and the measurements of ionic conductivity.

X-ray powder diffraction patterns were recorded for representative samples using a JEOL X-ray diffractometer Model No. JDX-8P with monochromatic Fe  $K\alpha$  ( $\lambda = 1.934 \text{ \AA}$ ) as the source. Single crystal Weissenberg photographs were also taken for some samples. The cell parameters for these new superionic triorthophosphates are given in table 1. The structures of the representative samples such as  $\text{Na}_2(\text{La}, \text{Al})\text{Zr}(\text{PO}_4)_3$  and  $\text{NaNi}_2\text{Zr}(\text{PO}_4)_3$  have been refined and will be reported elsewhere in detail. The structure consists of  $[\text{NaO}_6]$ ,  $[\text{MeO}_6]$ ,  $[\text{LaO}_6]$  and  $[\text{ZrO}_6]$  octahedra linked with  $[\text{PO}_4]$  tetrahedra to form a three-dimensional network with tunnels for the diffusion of Na ions. The introduction of Cu, Ni, Co, Cr, Al, La, Fe, etc. reduces the replacement of Zr by Na and the existence of free zirconia, and im-

proves the mechanical strength of the material. The DTA curves for representative samples of these new compounds show that the crystals undergo a phase transition around  $570^\circ\text{C}$  (except  $\text{NaCu}_2\text{Zr}(\text{PO}_4)_3$  which does not show any phase transition) and melt at temperatures around  $1000^\circ\text{C}$ .

Impedance measurements were carried out for  $\text{Na}_2(\text{La}, \text{Me}^{3+})\text{M}^{4+}(\text{PO}_4)_3$  and  $\text{NaMe}_2^{2+}\text{M}^{4+}(\text{PO}_4)_3$  crystals which were powdered and pressed into pellets by applying 5 ton/inch<sup>2</sup> pressure. The pellets (10 mm diameter, 3 mm thickness and 85–90% compactness) were provided with blocking silver electrodes on either side. These pellets were sintered in a vacuum chamber ( $10^{-2}$  Torr) at  $300^\circ\text{C}$  before measurement. Scanning electron microphotographs of the pellets, for example,  $\text{Na}_2(\text{La}, \text{Al})\text{Zr}(\text{PO}_4)_3$ , exhibit uniform grain size and relatively a low degree of porosity at grain boundaries (fig. 3). No microcracking was observed in any of the pellets. A capacitance bridge General Radio 1620-B was used in the present experiments. The preliminary ionic conductivity measurements were carried out at 1 kHz AC internal within the temperature interval  $25\text{--}300^\circ\text{C}$ .

Ionic conductivity in  $\text{Na}_2(\text{La}, \text{Me}^{3+})\text{M}^{4+}(\text{PO}_4)_3$  and  $\text{NaMe}_2^{2+}\text{M}^{4+}(\text{PO}_4)_3$  crystals was measured as a function of temperature and the corresponding Arrhenius plots of  $\ln \sigma T$  versus  $10^3/T$  are shown in figs. 4 and 5 for the representative samples, viz.  $\text{Na}_2(\text{La}, \text{Al})\text{Zr}(\text{PO}_4)_3$  and

Table 1  
Cell parameters for new triorthophosphates

Compound	System	Cell parameters ( $\text{\AA}$ )			Axial angles (deg)	Volume ( $\text{\AA}^3$ )
		<i>a</i>	<i>b</i>	<i>c</i>		
$\text{NaCu}_2\text{Zr}(\text{PO}_4)_3$	Tetragonal	5.04	—	3.57	—	90.68
$\text{NaNi}_2\text{Zr}(\text{PO}_4)_3$	Monoclinic	10.59	8.93	12.19	$\beta = 83.7$	560.80
$\text{NaMn}_2\text{Zr}(\text{PO}_4)_3$	Orthorhombic	9.29	7.17	6.05	—	402.96
$\text{Na}_2\text{LaZr}(\text{PO}_4)_3$	Triclinic	11.26	6.08	4.73	$\alpha = 84, \beta = \gamma = 90$	293.77
$\text{Na}_2(\text{La}, \text{Al})\text{Zr}(\text{PO}_4)_3$	Triclinic	10.07	6.43	5.57	$\alpha = 90, \beta = 87, \gamma = 84$	291.11
$\text{Na}_2(\text{La}, \text{Al})\text{Ti}(\text{PO}_4)_3$	Monoclinic	10.93	9.23	12.61	$\beta = 79$	310.65
$\text{Na}_2(\text{La}, \text{Cr})\text{Zr}(\text{PO}_4)_3$	Orthorhombic	11.57	6.96	3.64	—	293.98
$\text{Na}_2(\text{La}, \text{Co})\text{Zr}(\text{PO}_4)_3$	Triclinic	10.00	6.95	6.21	$\alpha = \beta = 90, \gamma = 85$	413.44
$\text{Na}_2(\text{La}, \text{Co})\text{Ti}(\text{PO}_4)_3$	Triclinic	8.50	7.17	6.73	$\alpha = \beta = 90, \gamma = 88$	410.72
$\text{Na}_2(\text{Ce}, \text{Co})\text{Zr}(\text{PO}_4)_3$	Triclinic	10.39	7.01	5.62	$\alpha = \beta = 90, \gamma = 84$	409.93
$\text{Na}_2(\text{Nd}, \text{Co})\text{Zr}(\text{PO}_4)_3$	Triclinic	9.62	6.94	6.08	$\alpha = \beta = 90, \gamma = 85$	405.31
$\text{Na}_2(\text{La}, \text{Fe})\text{Zr}(\text{PO}_4)_3$	Orthorhombic	9.28	7.22	3.97	—	263.98

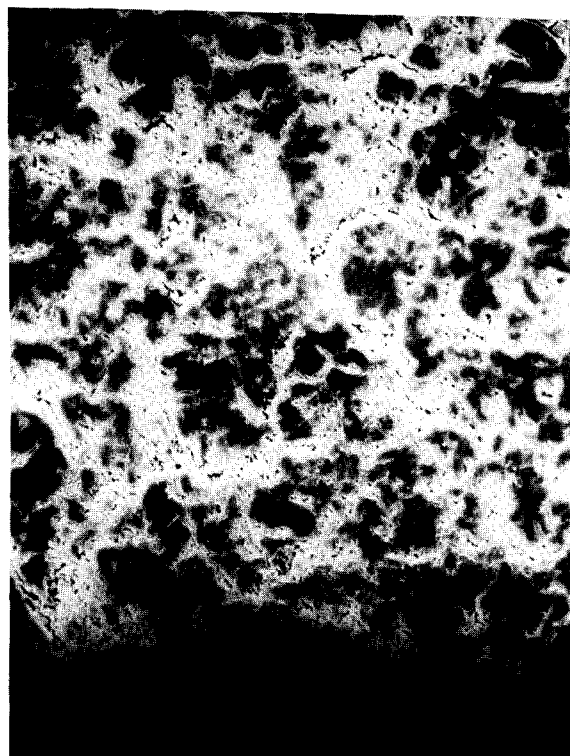


Fig. 3. SEM photograph of  $\text{Na}_2(\text{La, Al})\text{Zr}(\text{PO}_4)_3$  pellet.

$\text{NaCu}_2\text{Zr}(\text{PO}_4)_3$ . The corresponding values of the activation energy are 0.18 and 0.80 eV respectively. In general the activation energy values in

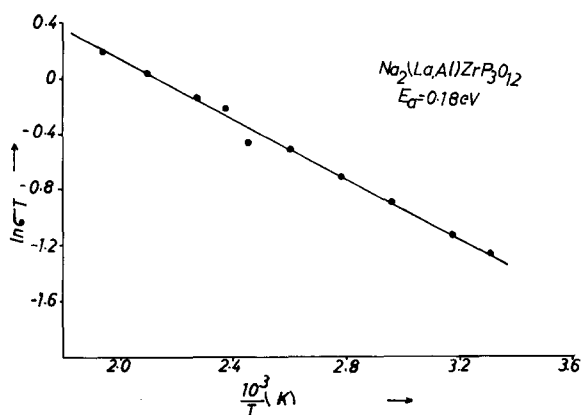


Fig. 4.  $\ln \sigma T$  versus  $10^3/T$  plot for  $\text{Na}_2(\text{La, Al})\text{Zr}(\text{PO}_4)_3$  crystals.

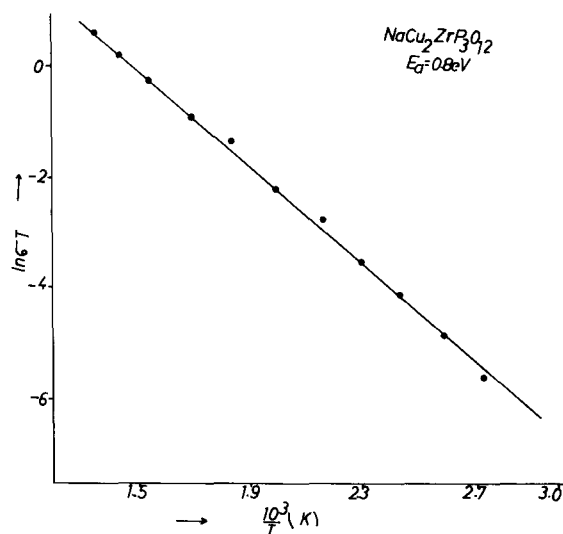


Fig. 5.  $\ln \sigma T$  versus  $10^3/T$  plot for  $\text{NaCu}_2\text{Zr}(\text{PO}_4)_3$  crystals.

these new superionic triorthophosphates range from 0.16 to 1.0 eV.

A complex impedance plot was constructed for  $\text{Na}_2(\text{La, Al})\text{Zr}(\text{PO}_4)_3$  at  $33^\circ\text{C}$  and it shows a clear semi-circle (at higher frequencies) and an inclined spike (at lower frequencies) indicating that significant grain boundary effects in the sample are absent.

In general, the ionic conductivity in these compounds was of the order of  $10^{-2}$  to  $10^{-1}$  ( $\text{ohm cm}^{-1}$ ) at  $300^\circ\text{C}$ . The titanium bearing compounds show lower values of ionic conductivity, for example,  $\text{Na}_2(\text{La, Al})\text{Ti}(\text{PO}_4)_3$  crystals show ionic conductivity values of the order of nearly  $1.40 \times 10^{-3}$  ( $\text{ohm cm}^{-1}$ ) at  $300^\circ\text{C}$ , and  $\text{NaNi}_2\text{Ti}(\text{PO}_4)_3$  shows the ionic conductivity values of the order of  $1.5 \times 10^{-4}$  ( $\text{ohm cm}^{-1}$ ) at  $300^\circ\text{C}$ . This may be because when smaller ions like Ti are introduced into the composition, the tunnel widths may increase and thereby decrease the ionic motion. In some cases an introduction of Ti instead of Zr into the composition of these triorthophosphates has changed the structure (table 1).

Thus the above studies confirm these new triorthophosphates as a new class of superionic conductors with potential.

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