

Crystal growth formation processes of HNaMP_2O_7 crystals under hydrothermal conditions

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New Na^+ superionic conductors HNaMP_2O_7 (where $M = \text{Co}, \text{Ni}, \text{Zn}, \text{Mn}, \text{Cu}, \text{Pb}$ or Fe) were obtained by hydrothermal methods at lower PT conditions ($T = 250^\circ\text{C}$, $P = 1000 \text{ Pa}$). The process of crystallization with respect to solute–solvent interactions and complexation have been studied. The crystals were characterized by X-ray diffraction (XRD), electron probe X-ray analysis (EPMA) and impedance spectroscopy.

1. Introduction

There has been a growing interest in the study of phosphates in the last two decades owing to their widespread application, e.g. piezoelectric, luminescent, ceramic, solid state laser and superionic, in modern technology. Na^+ superionic phosphates have been reported for the past 15 years or so. Most of these phosphates are usually ortho- or triorthophosphates, and the majority of their structures are directly related to $\text{Na}_5\text{ZrP}_3\text{O}_{12}$ [1]. Ag^+ superionic pyrophosphates were reported by Takahashi *et al.* [2]. Recently, high Na^+ ionic conductivity in mixed condensed phosphates with framework structures was reported for the first time [3–5]. The Na^+ superionic pyrophosphates were obtained by hydrothermal methods. The study of the complexation process with reference to solvent–solute interaction, is of great importance to the understanding of pyrophosphate crystallization. Reports on such studies are seldom found in the literature, especially for superionic phosphates. Here, the authors have made an attempt to study solvent–solute interaction, complexation and related physico–chemical aspects of crystallization.

2. Experimental procedure

HNaMP_2O_7 (where $M = \text{Co}, \text{Ni}, \text{Zn}, \text{Mn}, \text{Cu}, \text{Pb}$ or Fe) crystals were obtained by hydrothermal techniques. The hydrothermal growth of condensed phosphates is quite complicated [6, 7]. Experiments were carried out in Morey-type autoclaves. The autoclaves were provided with Teflon liners owing to the highly corrosive nature of the phosphorus. The experiments were carried out within the temperature range $200\text{--}300^\circ\text{C}$, and with a per cent fill of $60\text{--}80\%$. The starting materials, such as oxide/nitrate of cobalt, nickel, zinc, manganese, iron or copper (Analar grade, Reidel de Haen Ag, Germany, BDH, India), were taken into the Teflon liner and $85 \text{ vol}\% \text{ H}_3\text{PO}_4$ (Analar grade, Ranbaxy, India) was poured into it.

The alkaline component NaOH , (Analar grade, Wilson Laboratories, India) in the form of a molar solution with desired molarity, was used as solvent. The pH of the solutions was measured before and after the experimental run. Hydrothermal crystallization was carried out by spontaneous nucleation. The temperature of the furnace was slowly raised to control the rate of nucleation [8].

3. Synthesis

Crystal growth processes under hydrothermal conditions cannot be observed directly. A literature survey mainly yields experimental description and the growth aspects of various compounds, but not the actual processes. In fact, no theoretical basis for the hydrothermal processes has been fully established. The present authors have attempted to study the crystal growth processes involved in the growth of the title compounds under hydrothermal conditions.

In the hydrothermal system, water is the principal component with regard to the relative content of salts, acids, alkalis and others, which might serve as mineralizers; yet solubility of many inorganic materials may increase by adding a suitable mineralizer to the solution. Many inorganic ions, including $(\text{OH})^-$, Cl^- , F^- , S^{2-} , NH_4^+ , H^+ and WO_4^{2-} , act as effective mineralizers. The complexates formed by these mineralizers should not be stable, such that they themselves precipitate [9]. But, the number of solvents which are commonly used as the most effective solvent is quite limited, and one of the principal solvents is the hydroxide of alkali metals. It is essential to control the nucleation rate to obtain good quality crystals in case of spontaneous nucleation. In the present work the authors obtained good crystals of the title compounds by inducing thermal oscillation in the order of $\pm 10^\circ\text{C}$ around a predetermined temperature. In experiments without thermal oscillation the crystals obtained were small and the quality was also poor

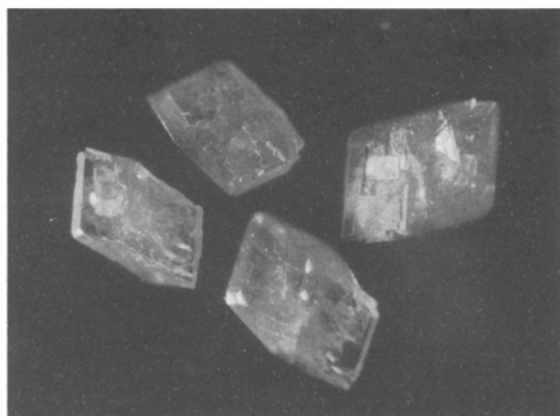
(Fig. 1a). On the contrary, crystals obtained in experiments with a moderate thermal oscillation in the order of $\pm 10^\circ\text{C}$, were relatively large in size and were also of improved quality (Fig. 1b).

In hydrothermal growth, analysis of the process usually starts with a study of the final crystal, and various hypotheses as to the manner in which the process takes place are derived from this.

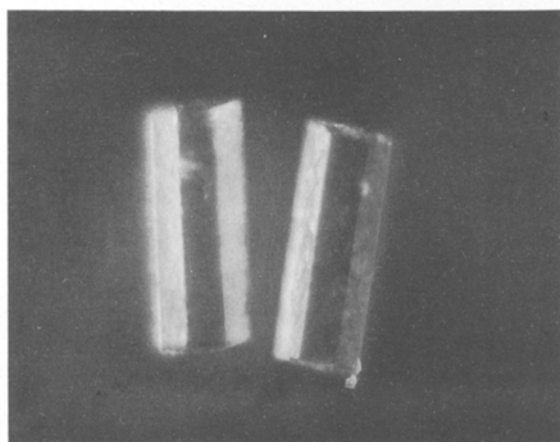
A full understanding of the complex system formed in solution is inconceivable without studying the effects of the solvent on the dissolved ionic species [10]. This depends on the behaviour of the solvent, which can be determined jointly by its general chemical and physical properties. These properties are involved in such a complex interaction that it is difficult to establish unambiguously how they contribute individually to the general behaviour of the solvents and its interaction with the solute. Here, the authors have used in all the experiments a mixture of 85 vol% H_3PO_4 and NaOH solution, of desired molarity, as the solvents. The oxide of divalent metals (or nitrate of Co, Ni, Zn, Cd, Mn, Fe or Cu) is considered as the solute.

The crystallization process involves many chemical interactions leading to the formation of a stable complex. To understand the growth of title compounds, the authors have described the following possible stages of interactions:

1. acid–base interactions,
2. formation of metal–aqua complexes, and



(a)



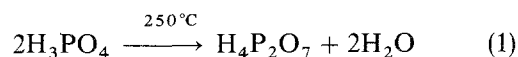
(b)

Figure 1 $\text{HNaCoP}_2\text{O}_7$ crystals obtained (a) without thermal oscillation ($\times 25$), and (b) with thermal oscillation ($\times 2.5$).

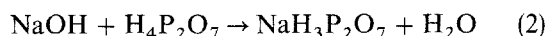
3. interaction between acid–base and metal–aqua complexes.

3.1. Acid–base interactions

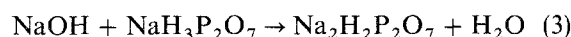
Components such as H_2O , OH^- and PO_4^{3-} are considered as the hard bases which act upon the dissolution of the solute, leading to the formation of sodium salts of orthophosphoric acid. But around 250°C , the amount of pyrophosphoric acid reaches its maximum [11]



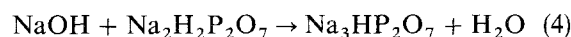
The interaction of pyrophosphoric acid and sodium hydroxide results in the formation of sodium salts of pyrophosphoric acid



As Equation 2 proceeds in a forward direction, the concentration of the water and the salt increases in the system. Consequently, the pH of the system also increases. As the pH increases the stability of $\text{NaH}_3\text{P}_2\text{O}_7$ decreases ($\text{pH} > 3$), and this leads to the formation of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$



The occurrence of Equation 3 also increases the pH of the system, but the compound $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ is stable in the pH range 3–9. The formation of $\text{Na}_3\text{HP}_2\text{O}_7$ is favoured if $\text{pH} > 9$

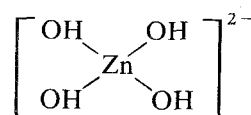


In all the experiments the pH was measured before and after the end of the experimental runs, and it was observed that the system was highly acidic ($\text{pH} = 2\text{--}3$). $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ is formed around pH 3, and it is more stable when $\text{pH} > 3$. Thus, interactions of the type shown in Equation 2 are expected to predominate in the present experimental runs followed by the type shown in Equation 3, and those of Equation 4 may be rare.

3.2. Formation of metal–aqua complexes

A literature survey of metal–aqua complexes in the hydrothermal system suggests that the complexes of zinc are studied in detail. The tendency of zinc towards a tetrahedral co-ordination is evidently responsible for the existence of $[\text{Zn}(\text{H}_2\text{O})_x(\text{OH})_{4-x}]^{x-2}$ type aqua complexes in aqueous solutions, where the value of x depends on the pH of the medium [12]. In strongly alkaline solutions, $\text{Zn}(\text{OH})_4^{2-}$ occurs (and here $x = 0$). On reducing the solution pH to neutral, a dizincate $[\text{Zn}_2\text{O}(\text{H}_2\text{O})_x(\text{OH})_{6-x}]^{x-4}$ may be formed as a result of the association of zincate ion.

The zinc oxide forms aqua complexes when dissolved in alkaline solutions [13]. The $\text{Zn}(\text{OH})_4^{2-}$ may have formed first



as the solution becomes dilute, Zn(OH)_2 , Zn(OH)_3^- and Zn(OH)_4^{2-} are stable [14]. The distribution of zinc aqua ions in alkaline solution is shown in Fig. 2.

Similar aqua complexes can be expected for the other divalent cations, like Mn^{2+} , Ni^{2+} , Fe^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} and others, under hydrothermal conditions.

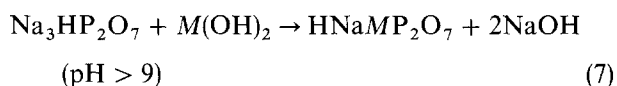
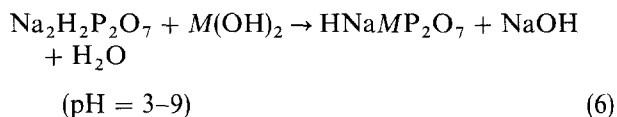
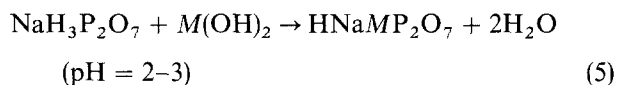
Although the metal cations form octahedral complexes, tetrahedral complexes are the more stable of the types of complexes. According to Jorgensen [15], a few octahedral complexes retain their constitution for a long time; Cu^{2+} , Cd^{2+} and Hg^{2+} have a half-life of aqua ligand around 10^{-9} s; whereas La^{3+} and Zn^{2+} have half-life of 3×10^{-8} s and Mg^{2+} has a half-life of around 10^{-5} s which is slightly more than for Co^{2+} , Fe^{2+} and Mn^{2+} . Thus, the conditions and number of octahedral aqua ions cannot be defined, and it is quite conceivable that it is not defined and that what is observed is the average stay of definite aqua ligand.

3.3. Interactions between acid–base and metal–aqua complexes

Pyrophosphoric acid forms salts due to the sequestering action of the pyrophosphate radical; the sequestering ability decreases with higher concentrations of salts, or with increasing pH. The sequestering ability is probably due to the geometry of the O–P–O–P–O chain, which is favourable to the adsorption of cations like Na^+ , Ca^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} and others. Na^+ ions compete with H^+ to form sodium salts of pyro-

phosphoric acid. The pH of the system determines the rate of formation and stability of these salts. Interactions between metal–aqua complexes with the sodium salts of pyrophosphoric acid lead to the formation of double salts of the type $\text{MM}'\text{P}_2\text{O}_7$, which can be formulated as the $\text{M}^+(\text{M}'\text{P}_2\text{O}_7)^-$ complex. Here, M is the alkali and M' is the transition metal ions. Here, the alkali metal will be electrostatically bonded to the complex. The $\text{M}'\text{–O–P}$ linkages are stronger because of their least partial covalent nature of bonding.

Hence, around 250°C and $\text{pH} = 2\text{--}3$, a reaction of the type shown in Equation 5, given below, is expected. Reactions of the type shown in Equations 6 and 7 may be rare



where $M = \text{Co, Ni, Zn, Cu, Mn, Pb}$ or Fe .

The aqua complexes can form more stable complexes because of the higher desolvation energy of metal cations when compared to sodium (3.97 eV).

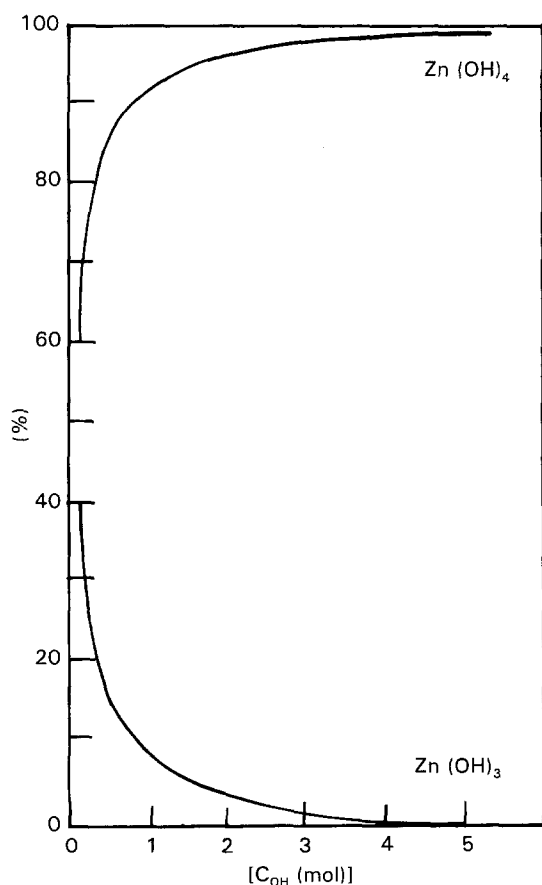


Figure 2 The distribution of zinc aqua ions with respect to the concentration of alkali solutions [14].

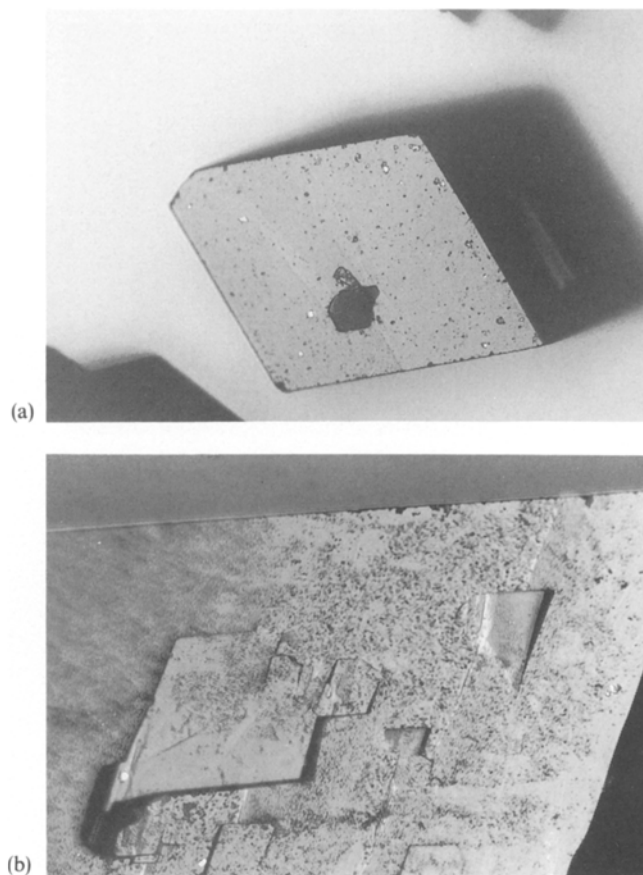


Figure 3 (a) Etch pits found on the (001) face of as-grown $\text{HNaCoP}_2\text{O}_7$ crystals ($\times 40$), and (b) block structures formed on the (001) face of as-grown $\text{HNaNiP}_2\text{O}_7$ crystals ($\times 40$).

TABLE I Cell parameters for new superionic pyrophosphates

Compound	System	Space group	Cell parameters (nm)			Axial angles	Volume (nm ³)
			<i>a</i>	<i>b</i>	<i>c</i>		
HNaMnP ₂ O ₇	Monoclinic	C ₂ /c	0.9935(4)	0.8455(3)	1.3106(4)	β = 110.75	102.900(1)
HNaCoP ₂ O ₇	Triclinic	P $\bar{1}$	0.6519(6)	0.6595(1)	0.6485(1)	α = 112.58(1) β = 92.07(1) γ = 83.85(1)	25.597(7)
Na ₂ CaMn(P ₂ O ₇) ₂	Triclinic	P $\bar{1}$	0.6657(3)	0.7372(4)	0.6517(3)	α = 122.66(1) β = 92.22(1) γ = 93.62(1)	26.925

Hence, formation of HNaMP₂O₇ is expected in the system instead of stable sodium salts of pyrophosphoric acid, namely Na₂H₂P₂O₇ and Na₄P₂O₇.

The authors have obtained good crystals up to 6 mm in size. The molar ratio of the starting components used in the growth of superionic pyrophosphates is Na₂O:MO:P₂O₅ = 10–12:4–4.5:35–40, where M = Co, Ni, Zn, Cu, Mn, Pb or Fe. Relatively smaller crystals were obtained in the case of Mn pyrophosphate, and bigger crystals in the case of Co pyrophosphate. The Mn pyrophosphate yields another phase, with the introduction of calcium in very small amounts in the nutrient composition. The electron probe micro analysis (EPMA, Cameca, SX-50, France) carried out on these samples showed the absence of Ca in the overall composition of the crystal, except for an insignificant concentration at the crystal periphery. However, single crystal X-ray diffraction studies have confirmed two different structures for the Mn pyrophosphate, and the results of the structural studies will be published elsewhere.

The experiments indicate that with surplus Na₂O in the nutrient composition, the viscosity of the starting mixture increases, and the crystals obtained are poor in quality. Experiments with pH < 2 show relatively more defect features, like etch pits and block structures, on the as-grown surfaces of the crystals (Fig. 3a, b). This corroborates the higher solubility of HNaMP₂O₇ in H₃PO₄, and also that the alkali metal pyrophosphates are more stable at pH > 3.

4. Characterization

The superionic pyrophosphates, HNaMP₂O₇ (where M = Co, Ni, Zn, Cu, Mn, Pb or Fe) were characterized by several, analytical methods like XRD, chemical analysis and impedance spectroscopy.

X-ray powder diffraction studies show that the resultant products were homogeneous in composition, and that these superionic pyrophosphates crystallized in the triclinic system, space group P $\bar{1}$. The cell parameters for the representative pyrophosphates are given in Table I.

Chemical analysis of representative samples of Na⁺ superionic pyrophosphates has been carried out using EPMA (SX-50, Cameca, France) and the results obtained are given in Table II.

The impedance measurements were carried out within a wide range of temperature and internal fre-

TABLE II The result of chemical analysis of superionic pyrophosphates by EPMA

Oxide	HNaCoP ₂ O ₇ (wt%)	HNaNiP ₂ O ₇ (wt%)	HNaZnP ₂ O ₇ (wt%)
Na ₂ O	09.92	11.67	11.42
CoO	30.67	00.10	00.10
ZrO ₂	00.00	00.00	00.00
P ₂ O ₅	59.45	58.18	57.94
ZnO	00.00	00.00	31.63
NiO	00.04	31.11	
MnO	00.12	00.25	00.21
CaO	00.04	00.00	00.00
FeO	00.04	00.22	00.04
TiO ₂	00.07	00.02	00.01
Total	100.35	101.56	101.25

quency for the representative crystal samples. The ionic conductivity for these superionic crystals varies at the order of 10⁻³–10⁻¹ Ω⁻¹ cm⁻¹ (at about 300 °C).

5. Conclusions

1. New superionic pyrophosphates HNaMP₂O₇, where M = Co, Ni, Zn, Cu, Mn, Pb or Fe, were obtained by hydrothermal methods within a wide range of PT conditions.

2. Simultaneous coexistence of pyrophosphate anions and metal–aqua complexes results in the crystallization of HNaMP₂O₇.

3. Higher desolvation energy of metal cations compared to that of sodium enables them to enter into the structure of HNaMP₂O₇.

4. The pH of the system is important in the formation of HNaMP₂O₇.

5. XRD studies show that the HNaMP₂O₇ crystals belong to the lower symmetry class, space group P $\bar{1}$ and C₂/c.

6. Impedance spectroscopic studies suggest that these compounds are perspective superionic conductors.

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