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Morphology of new superionic pyrophosphates

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New superionic pyrophosphates, $Na_2H_3Al(P_2O_7)_2$, $Na_2CaMn_2(P_2O_7)_2$, $NaFeP_2O_7$, $Na_2M^{2+}Zr(P_2O_7)_2$ where M = Mn, Co, Ni and Zn, and $(Na_{0.66}Zr_{0.33})_2P_2O_7$ were obtained by a hydrothermal method. The crystal growth, solubility and structure of these superionic pyrophosphates are discussed in brief. Detailed morphological studies were carried out with reference to the divalent/trivalent cations, degree of supersaturation, concentration of volatiles such as Na_2O, H_2O, P_2O_5 etc.

1. Introduction

Phosphates are the most important source material in several technological applications, and different groups of phosphates are used, for example, in piezoelectric, luminiscent, ceramic, solid state laser, and superionic applications. The synthesis of phosphates began in the last century [1] and continued up to the 1940s as a material attracting great interest, mainly in the study of morphological features. However, phosphates have been studied extensively over the last two decades, particularly since the generation of laser beams from NdP_5O_{14} [2], and the discovery of three-dimensional high ionic conductivity in NASICON during 1970s [3], as well as a host of other research [4–6]. Their morphology still attracts great interest; however, reports of morphological studies of superionic phosphates in the literature are almost absent, because superionic phosphates have only been reported over the last 15 years or so. Most of these phosphates are usually ortho- or triorthophosphates and the majority of their structures were directly related to $Na_3Sc_2P_3O_{12}$ [7]. Recently, high ionic conductivity in condensed phosphates (pyrophosphates $Na_2MZr(P_2O_7)_2$, where M = Ni, Co, Zn and Mn) was reported for the first time by our group [8–11]. Here, we report the morphology of these new supersonic pyrophosphates, $Na_2H_3Al(P_2O_7)_2$, $Na_2CaMn_2(P_2O_7)_2$, $NaFeP_2O_7$, $Na_2MZr(P_2O_7)_2$ where M = Mn, Co, Ni and Zn and $(Na_{0.66}Zr_{0.33})_2P_2O_7$.

2. Crystal growth

The growth of condensed phosphates by a hydrothermal method is quite complicated and relatively recent [12, 13], and the technology for pure phosphates has yet to be understood precisely. The experiments were carried out in Morey-type autoclaves provided with teflon liners within the temperature range 200–300 °C and in the pressure range 100–250 atm. The starting materials, such as oxides/nitrates of aluminium, calcium, manganese, iron, cobalt, nickel, zinc and zirconium were taken in a teflon liner and 85% H_3PO_4 was poured into it. The alkaline component of the starting materials was used in the form of a molar solution with a definite molarity and this solution acts as a mineralizer. Using this method the following new superionic pyrophosphates have been obtained: $(Na_{0.66}Zr_{0.33})_2P_2O_7$, $Na_2H_3Al(P_2O_7)_2$, $Na_2CaMn_2(P_2O_7)_2$, $Na_2MnZr(P_2O_7)_2$, $NaFeP_2O_7$, $Na_2CoZr(P_2O_7)_2$, $Na_2NiZr(P_2O_7)_2$, $Na_2ZnZr(P_2O_7)_2$.

Crystallization was carried out by spontaneous nucleation and the temperature of the furnace was slowly raised to control the rate of nucleation [14]. The crystals obtained by this method were of excellent quality showing vitreous lustre and the size varied from 0.5–6 mm. The molar ratios of the starting components with reference to the growth of new pyrophosphates are given in Table I.

3. Crystal morphology

The habit of a crystal is determined by the slowest growing faces having the lowest surface energy, but it is also apparent that a crystal habit is governed by kinetics rather than equilibrium considerations [15]. A number of factors, such as degree of supersaturation, type of solvent, pH of the mineralizer, etc., affect the habit of a crystal. Kern [16] showed that in a number of experiments, many ionic crystals change their habits when supersaturation exceeds a certain critical value. Wells [17] observed that a change in solvent results in a change in crystal habit. Sometimes the pH of gels has a considerable influence

TABLE I Nutrient ratio for superionic pyrophosphates

Compound	Molar ratio
$Na_2H_3Al(P_2O_7)_2$	$Na_2O:Al_2O_3:P_2O_5$ = 10–12:3–5:30–35
$Na_2MZr(P_2O_7)_2$ (M = Co, Ni, Zn, Mn)	$Na_2O:MO:ZrO_2:P_2O_5$ = 10–11:4–4.5:1:35–40
$NaFeP_2O_7$	$Na_2O:Fe_2O_3:P_2O_5$ = 4:1:8–10
$Na_2CaMn_2P_2O_7$	$Na_2O:MnO:CaO:P_2O_5$ = 8–10:3–4:1:25–30
$(Na_{0.66}Zr_{0.33})_2P_2O_7$	$Na_2O:ZrO_2:P_2O_5$ = 4–5:1:10–12

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on the growth rate of crystals, which ultimately changes the growth habit [18, 19]. Habit modifications are also observed when significant changes in the growth temperature and occurrence of impurities, because an increase in temperature increases the growth rates [20–22]. The most common cause of habit change is the presence of impurities in the crystallizing solution [23]. It is observed that even very small traces (0.01%) are enough to produce significant habit changes. Therefore, many observed crystal habits may be caused by unsuspected impurity effects. This is true with these pyrophosphates, which

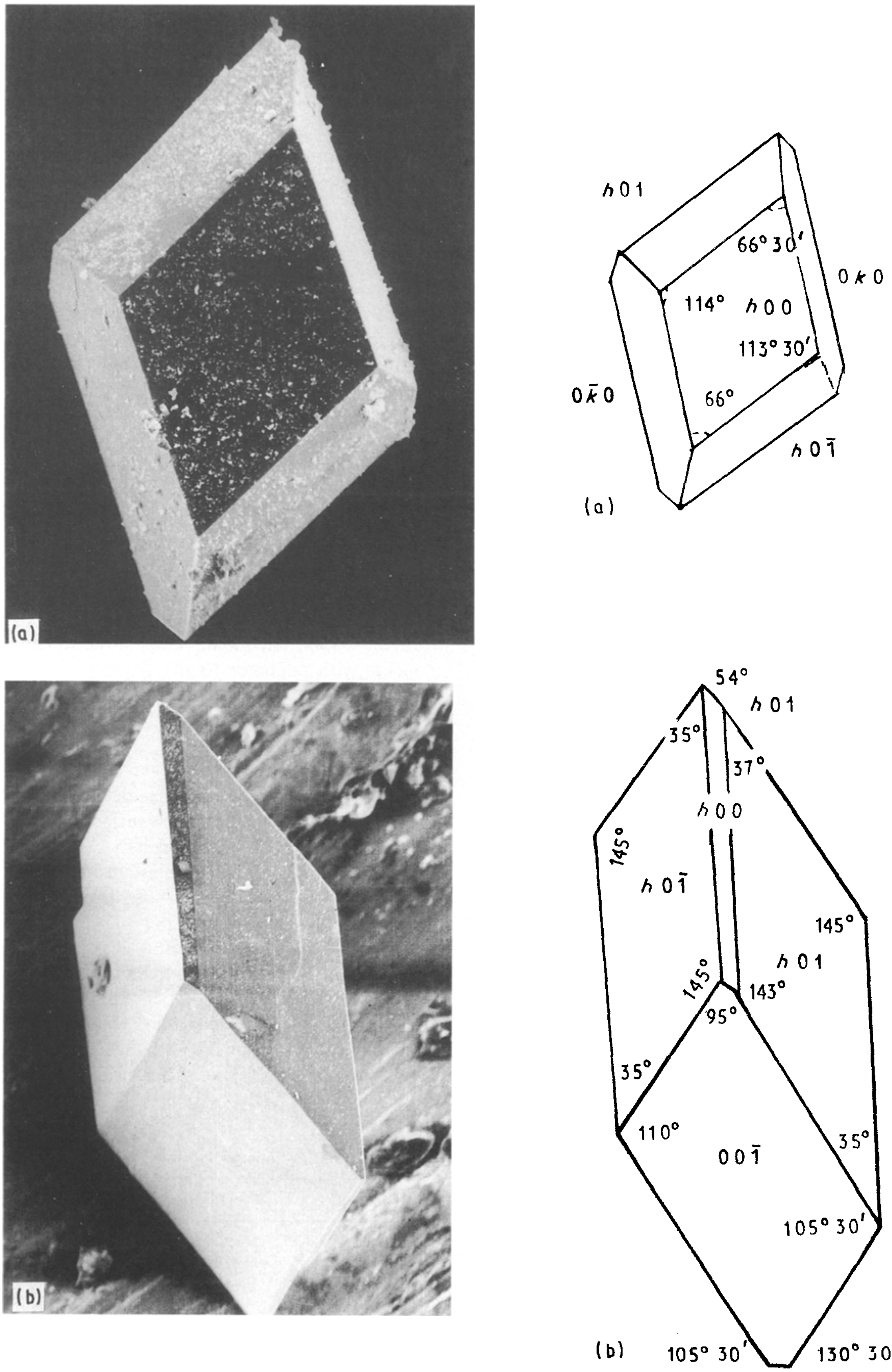


Figure 1 Representative photographs of the superionic pyrophosphates (a) $Na_2H_3Al(P_2O_7)_2$ (×25), (b) $Na_2CoZr(P_2O_7)_2$ (×40), (c) $Na_2NiZr(P_2O_7)_2$ (×25), (d) $(Na_{0.66}Zr_{0.33})_2P_2O_7$, (×40), (e) $Na_2CaMn_2(P_2O_7)$ (×40).

show a wide range of morphological variations not only due to the changes in the growth parameters but also due to the deliberate or accidental entry of dopants.

The morphology of these superionic pyrophosphates is very interesting and it is shown together with their schematic diagrams in Fig. 1a–e. The crystallization was carried out by spontaneous nucleation, which was controlled by a systematic rate of heating. Hence, the crystals were well developed and of excellent quality.

The X-ray diffraction studies (both powder and single-crystal) show that these crystals belong to the lower symmetry. The cell parameters for these new superionic pyrophosphates are given in Table II. Because these crystals belong to the lower symmetry, they show very interesting morphology. A general morphology of these pyrophosphates is given in Table III.

In order to grow these crystals, it is very important to know their solubility, internal atomic structure and macro- and micromorphology. The solubility of these pyrophosphates was found to be positive. Similarly, the crystals obtained by the hydrothermal technique show very interesting morphology. Hence, it becomes rather easy to grow them as bulk single crystals of several centimetres in length, despite the phosphoric acid media in which the growth occurs.

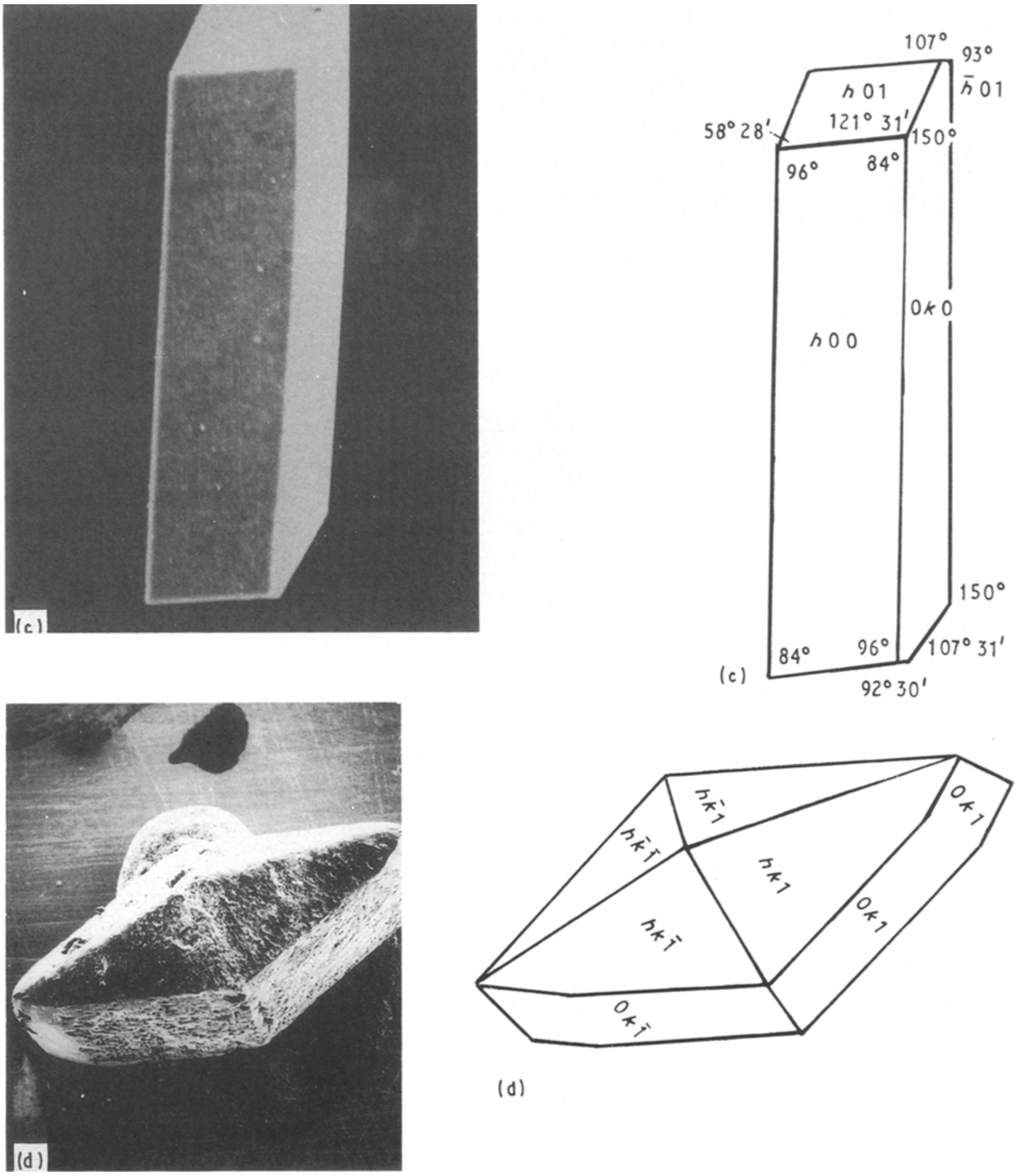


Figure 1 Continued.

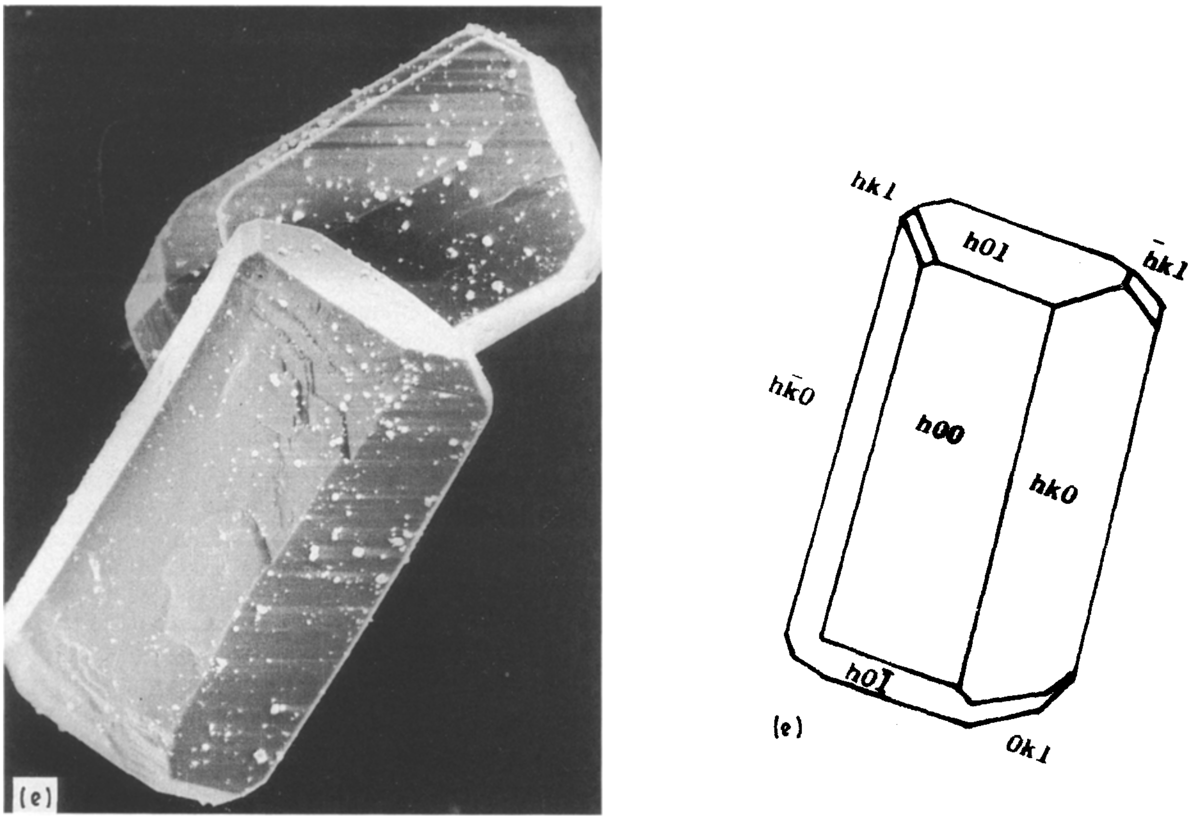


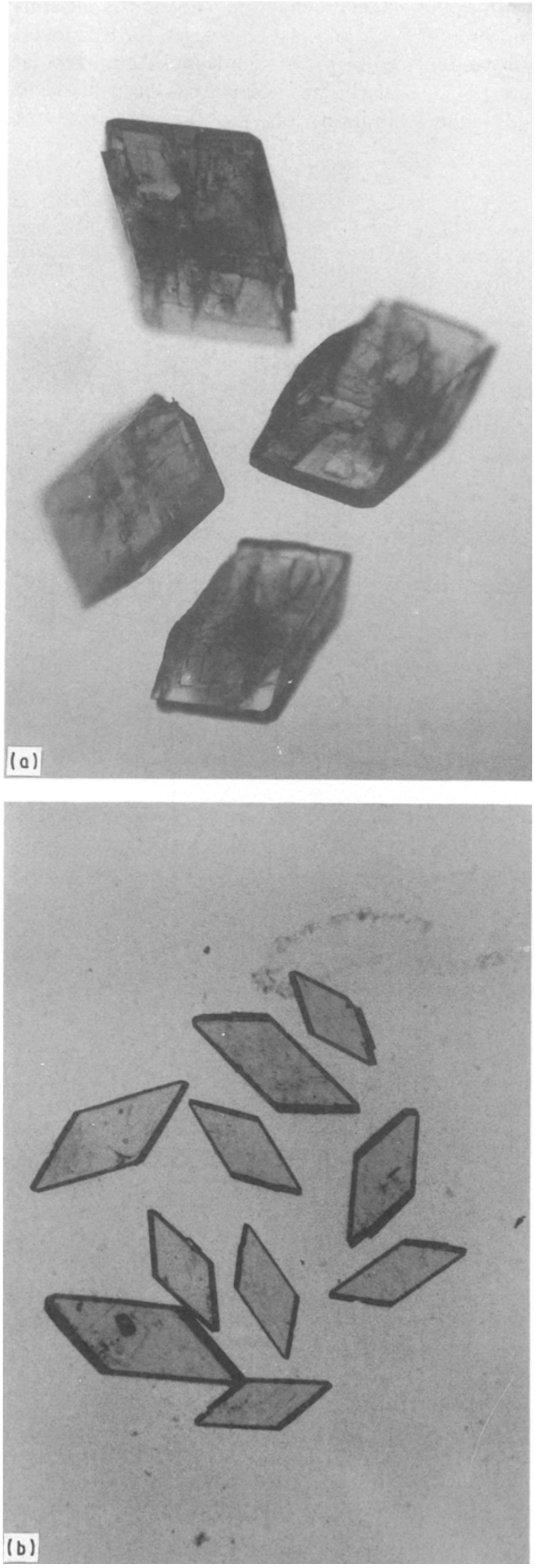
Figure 1 Continued.

TABLE II Cell parameters for new superionic pyrophosphates

Compound	System	Space group	Cell parameters (nm) *a*	*b*	*c*	Axial angles (deg)	Volume (nm^3)
$(Na_{0.66}Zr_{0.33})_2P_2O_7$	Orthorhombic	$\bar{1}$	0.6867 (5)	1.2345 (4)	2.7527 (5)	—	2.333 (2)
$Na_2H_3Al(P_2O_7)_2$	Triclinic	P1	0.8311	0.7363	0.4902	α = 99.665 (1)	
						β = 81.788 (1)	0.29577
						γ = 114.476 (1)	
$Na_2MnZr(P_2O_7)_2$	Triclinic	Pl	0.6420 (3)	0.7237 (4)	0.6487 (2)	α = 123.14 (1)	
						β = 91.92 (1)	0.2524
						γ = 93.79 (1)	
$NaFeP_2O_7$	Monoclinic	C2/c	1.183 (2)	1.2527 (6)	0.644 (1)	β = 114.18 (6)	0.87063
$Na_2CoZr(P_2O_7)_2$	Triclinic	Pl	0.6535 (3)	0.7266 (4)	0.6496 (3)	α = 122.96 (2)	
						β = 92.28 (2)	0.2572 (1)
						γ = 93.75 (2)	
$Na_2NiZr(P_2O_7)_2$	Triclinic	Pl	0.6461 (3)	0.7257 (4)	0.6501 (3)	α = 123.24 (1)	
						β = 91.95 (1)	0.2535 (1)
						γ = 93.79 (1)	
$Na_2ZnZr(P_2O_7)_2$	Triclinic	Pl	0.6457 (3)	0.7316 (4)	0.6500 (3)	α = 122.98 (1)	
						β = 92.09 (1)	0.25758
						γ = 93.45 (1)	
$Na_2CaMn(P_2O_7)_2$	Triclinic	Pl	0.6657 (3)	0.7372 (4)	0.6517 (3)	α = 122.66 (1)	
						β = 92.22 (1)	0.26925
						γ = 93.62 (1)	

TABLE III Morphology of pyrophosphates with cations

Element	Compound	Crystal symmetry/system	Morphology/habit
Al	$Na_2H_3Al(P_2O_7)_2$	Triclinic (P1)	Tabular, rhombohedral,
Mn	$Na_2MnZr(P_2O_7)_2$ $Na_2CaMn_2(P_2O_7)_2$	Triclinic (P1)	Rod, prismatic
Fe	$NaFeP_2O_7$	Monoclinic (C2/c)	Long needles
Co	$Na_2CoZr(P_2O_7)_2$	Triclinic (P1)	Perfect rhombohedral, prismatic, rod shaped
Ni	$Na_2NiZr(P_2O_7)_2$	Triclinic (P1)	Prismatic, rod shaped
Zn	$Na_2ZnZr(P_2O_7)_2$	Triclinic (P1)	Prismatic, needles
–	$(Na_{0.66}Zr_{0.33})_2P_2O_7$	Orthorhombic (I)	Dome shaped, tabular



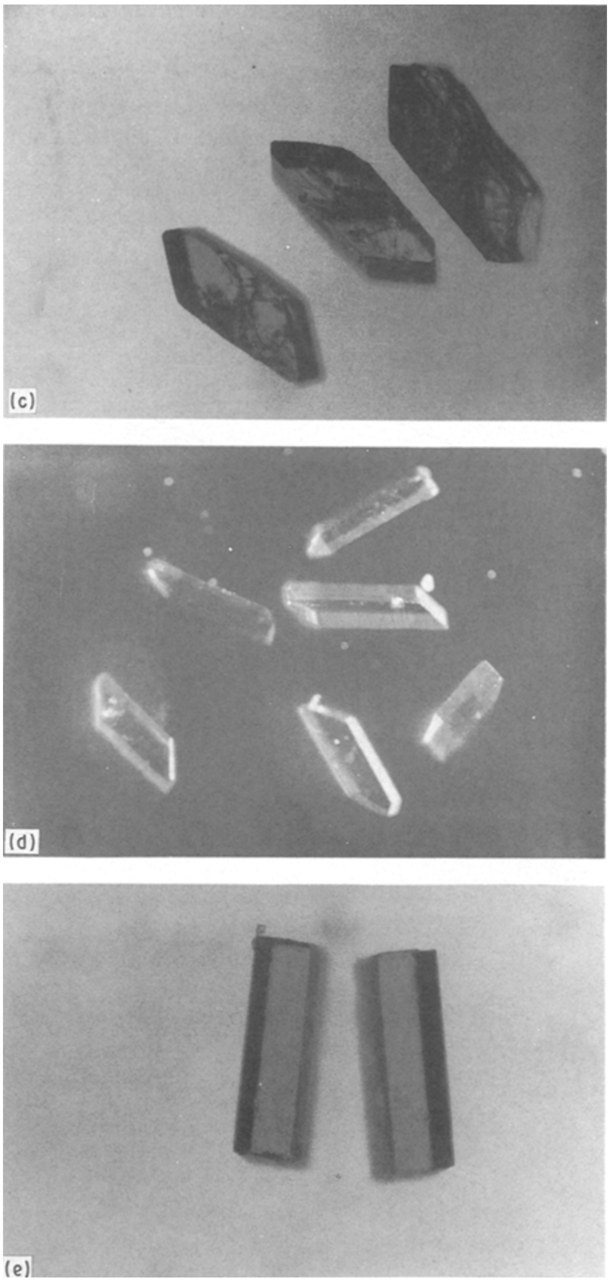


Figure 2 (a–e) Variation in the morphology of $Na_2CoZr(P_2O_7)_2$ with variation of P_2O_5 content in the system (× 10).

The most common morphological habits observed in pyrophosphates are perfect rhombohedral, prismatic, rod shaped, etc. The crystal faces are more or less smooth and vitreous in lustre, with a high degree of transparency. The prism faces dominated over all other faces in all the crystals followed by pinacoidal and dome faces. There is a clear-cut distinction in the morphology of these pyrophosphates. Characteristic photographs of $Na_2CoZr(P_2O_7)_2$ are shown in Fig. 2a–e. In most of the experiments the entry of the selective dopants was controlled in order to observe the morphological variations. The morphology of these pyrophosphates varies from one to another, depending on the cations present.

To gain an understanding of the morphological variation with respect to the growth conditions, it is essential to study particularly the role of the degree of supersaturation, the concentration of water and Na_2O in the system. $Na_2CoZr(P_2O_7)_2$ and $Na_2ZnZr(P_2O_7)_2$ crystals were selected for such a systematic study, because these compounds show a very well-developed morphology and are sensitive to such variations. In fact, both these compounds show similar morphological variations. Fig. 2a–e show how the morphology varies with the concentration of P_2O_5. This is further represented in the schematic diagram (Fig. 3). The interfacial angles for the representative pyrophosphates have been measured using a Leitz phase-contrast microscope and these angles are shown in the schematic diagrams (Fig. 3). As the concentration of P_2O_5 and H_2O increases, the pyramidal faces are replaced by the prismatic and the pinacoidal faces [24]. Similarly, an attempt has been made to study the variation of the growth rate of

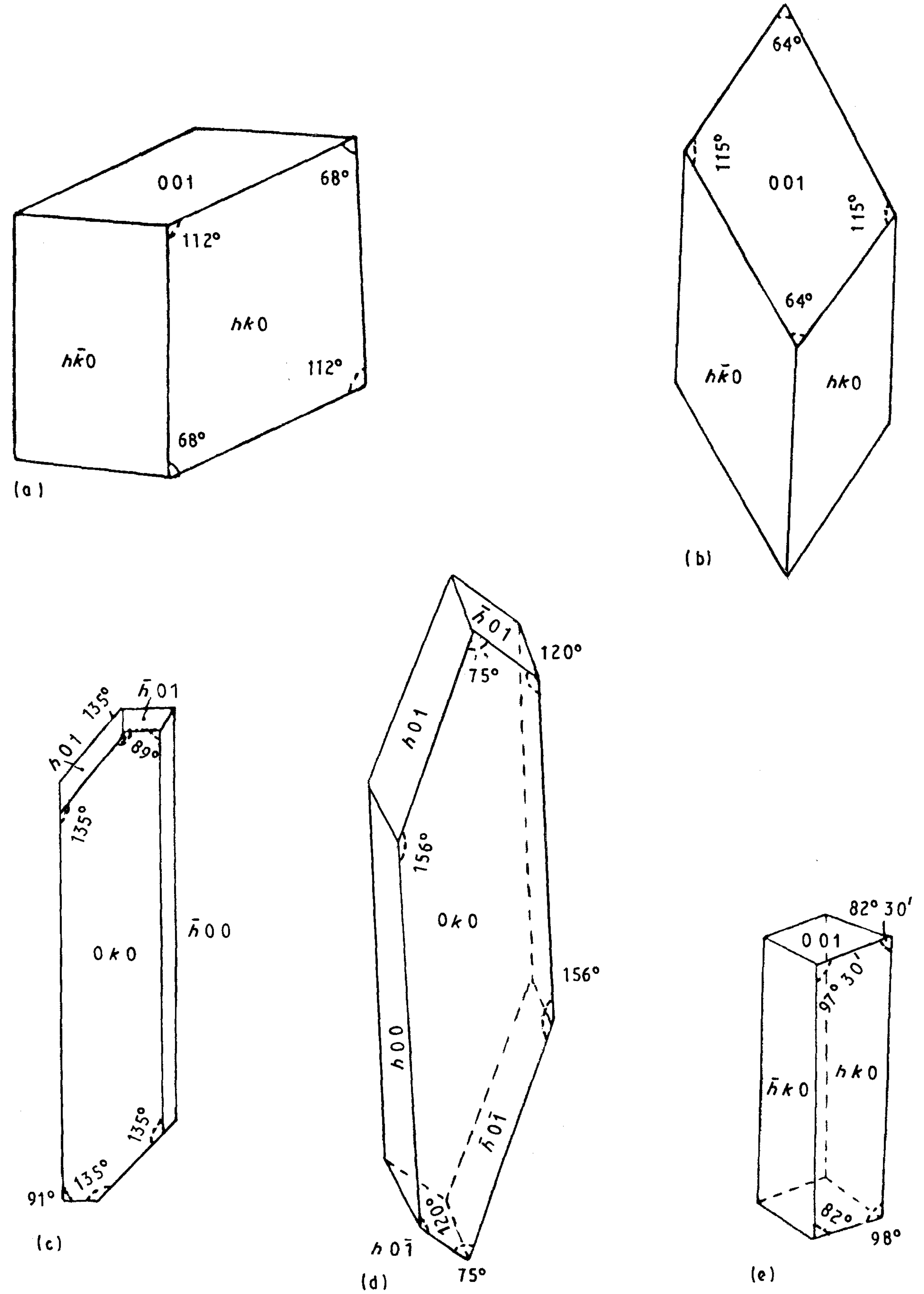
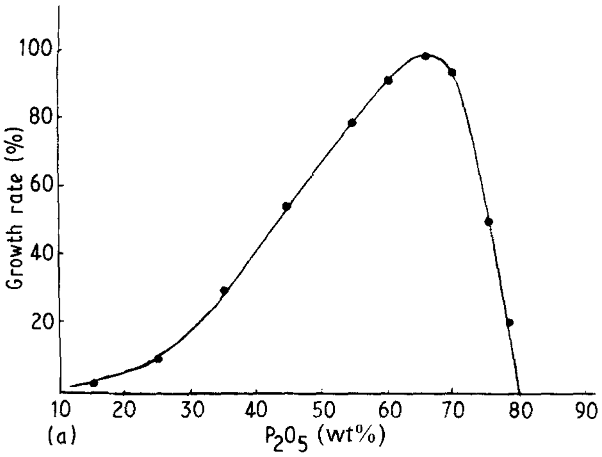
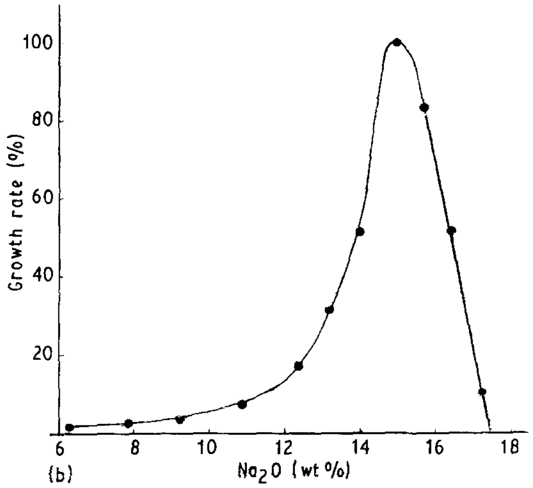


Figure 3 Schematic diagram of the crystals represented in Fig. 2.





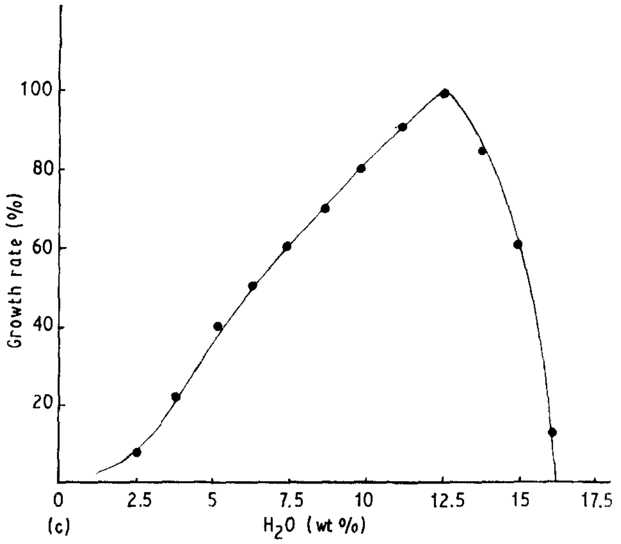


Figure 4 (a) Growth rate of $Na_2CoZr(P_2O_7)_2$ versus P_2O_5 concentration. (b) Growth rate of $Na_2CoZr(P_2O_7)_2$ versus Na_2O concentration. (c) Growth rate of $Na_2CoZr(P_2O_7)_2$ versus H_2O concentration.

$Na_2CoZr(P_2O_7)_2$ crystals with concentration of P_2O_5, Na_2O and H_2O (Fig. 4a–c). These figures show critical points beyond which the growth rate falls sharply. This helps to fix the optimum conditions for the growth of $Na_2CoZr(P_2O_7)_2$ [24].

Similar features were observed in the case of $Na_2ZnZr(P_2O_7)_2$ crystals. Representative photographs (Fig. 5a–d) of $Na_2ZnZr(P_2O_7)_2$ show how the morphology varies with the above-mentioned growth parameters.

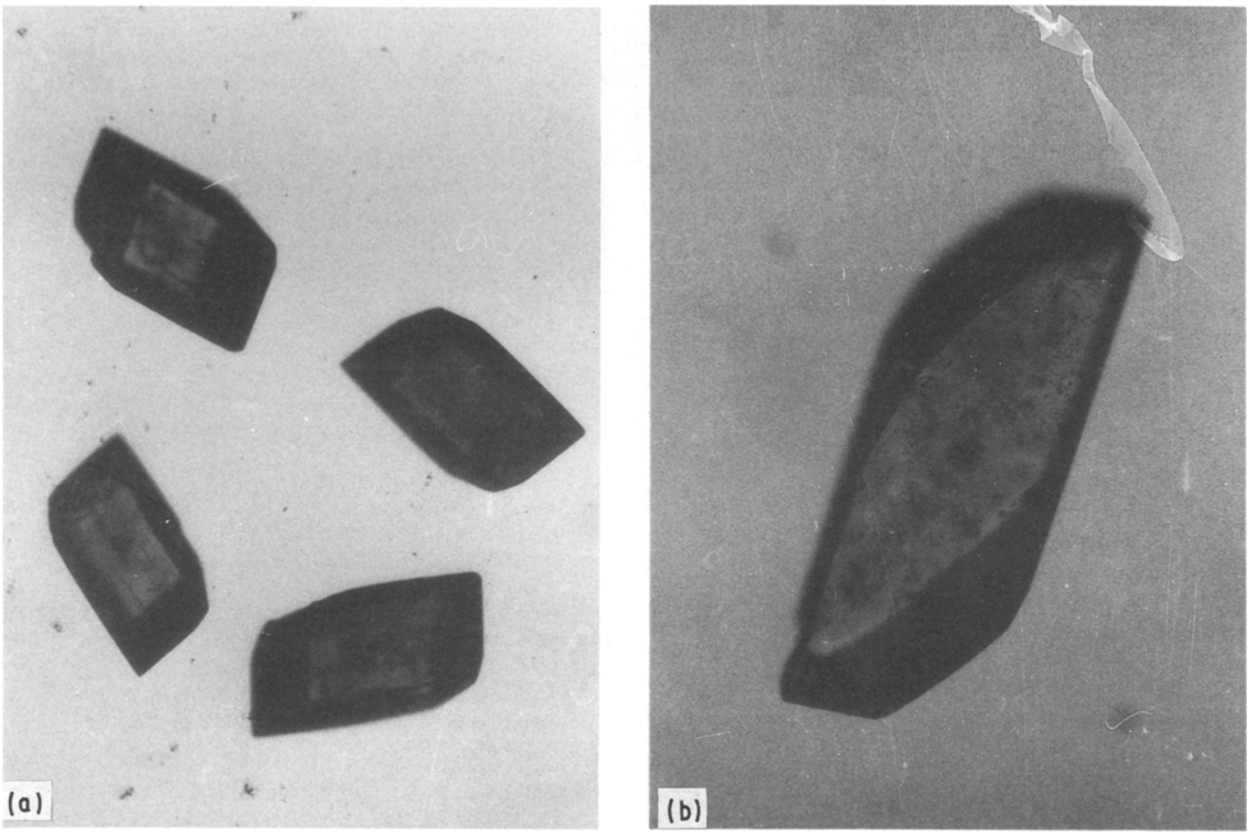


Figure 5 Representative photograph of $Na_2ZnZr(P_2O_7)_2$ crystals showing variation in the morphology with reference to the concentration of P_2O_5 in the system: a = c (× 10), d (× 6).

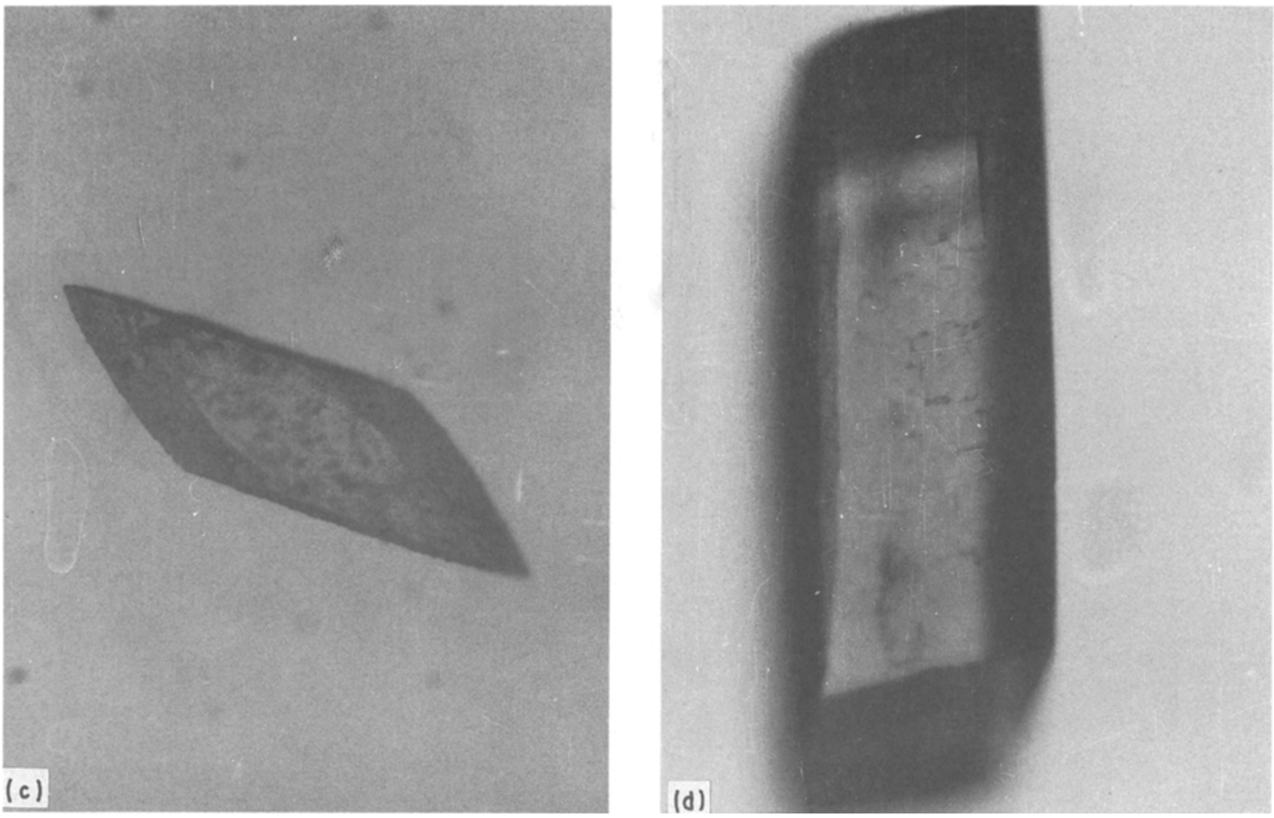


Figure 5 Continued.

These experiments indicate that the degree of supersaturation, concentration of cations and dopants determine the morphology of these pyrophosphates. Such studies help in the successful growth of superionic phosphates in the form of single crystals with a desired morphology.

4. Conclusion

New group of superionic pyrophosphates were obtained by a hydrothermal technique. The morphology of these pyrophosphates depends upon the cations, degree of supersaturation, dopants and volatile concentrations, etc. On the whole, the overall morphologies are closely interrelated with one another.

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