

Crystallization of aluminium orthophosphate

K. BYRAPPA, V. VENKATACHALAPATHY, B. PUTTARAJ

The Mineralogical Institute, University of Mysore, Manasa Gangotri, Mysore 570006 India

Aluminium orthophosphate crystals were crystallized by a hydrothermal technique using various solvents. The influence of nutrient materials and solvents on the rate of crystallization, solubility, morphology and quality of the crystals was studied. The crystals obtained were subjected to analysis by X-ray diffraction (XRD), scanning electron microscopy (SEM) and IR spectroscopy.

1. Introduction

Aluminium orthophosphate — berlinite — is of particular interest for materials scientists because of its large mechanical coupling factors, greater than α -quartz, which are suitable for both bulk and surface wave applications. Aluminium orthophosphate is therefore popular as a possible substitute for α -quartz in piezoelectric device applications. In 1953 Jahn and Kordes reported on the growth of AlPO_4 based on a temperature coefficient of solubility which was positive [1]. Stanley has successfully grown single crystals of aluminium orthophosphate in the temperature range 132 to 315°C by a hydrothermal technique [2]. He carried out the experiments in sealed borosilicate glass vessels placed in low pressure autoclaves. However, the study of the growth of aluminium orthophosphate in the form of single crystals and the study of phase equilibria in phosphate systems ceased for various reasons. Only recently has the study of the growth of aluminium orthophosphate and the study of phosphate systems become popular.

In 1978 Croxall *et al.*, Belt *et al.* and Kolb *et al.* came out with their reports on the growth and assessment of aluminium orthophosphate using different techniques [3–5]. Today there is a large number of reports on berlinite crystals available and there are many laboratories throughout the world working on the growth and characterization of berlinite crystals. It is presumed that studying the growth of berlinite crystals was not popular in the past because of the lack of growth technology. Even today scientists are unable to understand completely the technology of the growth of berlinite as large single crystals. The dielectric

constant for berlinite was determined by Mason in 1950 [6] and since then there has been a considerable improvement in crystal size and quality. There are a great many reports on the dielectric constants of berlinite. However, there are significant differences between the results reported by different researchers, which may be due to the variations in experimental methods. The present paper deals with the effects of the starting materials, temperature of growth, and the solvent on the crystallization, rate of growth, morphology, crystal size and solubility of berlinite single crystals. Special attention has been paid to the solvent used and its effect on the morphology and quality of crystals. The characterization of berlinite single crystals was carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM) and IR spectroscopy.

2. Experimental methods

Berlinite crystals can be obtained by various growth techniques: from aqueous phosphoric acid solution, the direct crystallization technique and the hydrothermal technique. Several growth techniques based on direct crystallization have been examined, but the best quality crystals have been grown under static temperature gradient conditions [3]. In case of growth from aqueous phosphoric acid solution AlPO_4 crystals were obtained by slowly raising the temperature of the solution saturated with an aluminous compound, such as aluminium oxide, aluminium hydroxide, sodium aluminate, etc. A slow raising of the temperature is found to be effective in growing berlinite crystals since berlinite has a negative temperature coefficient of solubility.

TABLE I Experimental conditions

Nutrient composition		Temperature (°C)	Pressure (p.s.i.)	Duration (days)	Remarks
H ₃ PO ₄	6 ml	280	2000	5	Well developed hexagonal crystals
Al ₂ O ₃	3 g				
NH ₄ Cl (4M)	10 ml				
H ₃ PO ₄	5 ml	300	2000	5	Large hexagonal crystals
Al ₂ O ₃	4 g				
NaCl (2M)	10 ml				
H ₃ PO ₄	5 ml	300	2000	6	Rod-shaped, needles and ascicular crystals
Al(OH) ₃	3 g				
HCl (2M)	15 ml				
H ₃ PO ₄	6 ml	300	2000	5	Hexagonal and equi-dimensional crystals
Al ₂ O ₃	4 g				
HCOOH (2M)	14 ml				
H ₃ PO ₄	7 ml	280	2000	5	Rhombohedral and hexagonal crystals
Al ₂ O ₃	4 g				
NaHCO ₃ (3M)	18 ml				

The experiments reported in this paper were carried out by the hydrothermal technique using teflon liners. It is well known that orthophosphoric acid is highly corrosive at higher temperatures, and therefore it is not advisable to carry out the growth experiments in platinum liners for experiments of long duration. This has been well corroborated in the case of experiments on rare-earth phosphates [7]. Here, it was found that irrespective of which metals (such as platinum, cobalt, nickel, gold and irridium) were used in the experiments, the resultant product contained the crucible material in small concentrations. It is well known that these metals can form stable tetrahedral or octahedral complexes in phosphoric acid solutions under suitable conditions. They exist as structural admixtures in berlinite. It is hard to understand the existence of these strong complexes in the crystal framework according to the current stereochemical understanding. A detailed study of the existence of admixtures and their influence on the general properties of berlinite and its crystallization will be reported elsewhere. It is advisable to carry out the experiments using vitreous carbon glass liners or teflon liners.

The authors carried out the experiments reported here, in Morey-type autoclaves of capacity 25 to 50 ml using teflon liners. The temperature range was 200 to 300°C and the pressure range 200 p.s.i. to 10 kp.s.i. in order to crystallize AlPO₄ monocrystals. These autoclaves are

normally provided with a safety blow-out disc. The per cent fill of the liners and the experimental temperatures were used in calculating the pressure. The temperature of the furnace was controlled using a controller and a programmer. The starting materials were placed at the top in a perforated teflon gasket. A small gradient was maintained between the growth zone and nutrient zone. The experiments were carried out by spontaneous crystallization without using seeds. The starting materials such as aluminium oxide, aluminium hydroxide or sodium aluminite were taken in a teflon liner and 85% orthophosphoric acid was poured into it. The mineralizer solution was taken with a definite molarity. Since the crystallization occurred by spontaneous nucleation, the temperature of the furnace was slowly increased to control the rate of nucleation. When the rate of heating was 5°C h⁻¹, the rate of crystallization was quite high. At the higher rate of heating the quality of the crystals was good, and they ranged in size from 1 to 3 mm. When the heating rate was 15°C h⁻¹ the crystals were quite large, but the quality was poor and they were mostly equi-dimensional. The experimental details are given in Table I.

In the majority of the experiments, the per cent fill ranged from 70 to 85%. The experimental temperature ranged from 200 to 320°C. The growth rate was quite high at elevated temperatures, irrespective of the nutrient material with

TABLE II Experimental conditions

Nutrient composition	Per cent fill	Temperature (° C)	Time (days)	Size of crystals (mm)
Al ₂ O ₃ + H ₃ PO ₄ mineralizer NH ₄ Cl	82	300	7	0.5–1.5
Al ₂ O ₃ + H ₃ PO ₄ mineralizer NaCl	78	300	7	0.5–2.0
Al(OH) ₃ + H ₃ PO ₄ mineralizer HCl	80	300	7	1.0–3.0
Al ₂ O ₃ + H ₃ PO ₄ mineralizer HCOOH	80	300	7	0.5–2.5
Al ₂ O ₃ + H ₃ PO ₄ mineralizer NaHCO ₃	80	300	7	0.5–1.5

a few exceptions. Good quality crystals were obtained when the per cent fill was 80% and the growth temperature was 300°C. The experiments normally were carried out for 5 days and the crystals resulted from spontaneous crystallization. Therefore the crystals were quite small in size in these experiments. Both the size and the quality of the crystals depend upon the growth temperature, per cent fill, nutrient material used and mineralizer in action. Details of the size, per cent fill and the nutrient material are given in Table II.

The authors tried a few runs with small grains of natural quartz as the seed material in an attempt to crystallize berlinite epitaxially over quartz. Since both quartz and berlinite have got the same crystalline structure, it is very interesting to study the boundary layer, and it is also presumed that aluminium orthophosphate crystallized over a quartz crystal will be of great interest in piezoelectric devices. With this aim, the authors conducted some experiments and the results obtained were encouraging. The quartz grains were kept at the bottom and the nutrient material was kept at the top in a perforated teflon gasket. A detailed report on this will be published elsewhere.

3. Hydrothermal solvent

There are many reports on the effects of various hydrothermal solvents and growth temperatures on the solubility of aluminium orthophosphate [3–5, 8]. According to the assessment of the present authors the solubility data given by various other authors differ slightly with one another. An attempt has been made to study the solubility of AlPO₄ in some new hydrothermal solvents such as HCOOH and NH₄Cl. The solubility measurements were carried out by the weight loss method. Here, a crystal is kept in equilibrium with an appropriate solution at the desired pressure and temperature conditions for a period of time greater than that necessary to establish equilibrium. The solubility of AlPO₄ (in wt %) as a function of temperature and at a pressure of 2 kp.s.i. in 2M

HCOOH solution is shown in Fig. 1. The slope of the solubility curve for AlPO₄ in HCOOH is similar to the solubility curves of AlPO₄ in HCl and H₃PO₄ [8]. Kolb *et al.* have determined the solubility of AlPO₄ in various solvents [8]. The present work gives data additional to the previous work [8]. A comparison of the data is given in Table III. Some new solvents, including NH₄H₂PO₄, NH₄Cl, HCOOH, KF, NaF, LiF, NaHCO₃ and KHCO₃, have been tried. Good quality crystals were obtained in case of 2M HCOOH and 3M HCOOH, and similarly in NaF and NH₄Cl. In all these cases the growth rate was fairly high, particularly in the case of NH₄Cl. All these solvents can be considered as promising new hydrothermal solvents in the growth of AlPO₄ crystals. The solubility was quite high in all cases, AlPO₄ was a stable phase and crystals were always transparent and consisted of well developed faces. These experiments can be improved and applied to grow large single crystals using the seed technique.

Aluminium orthophosphate shows a negative temperature coefficient of solubility and therefore

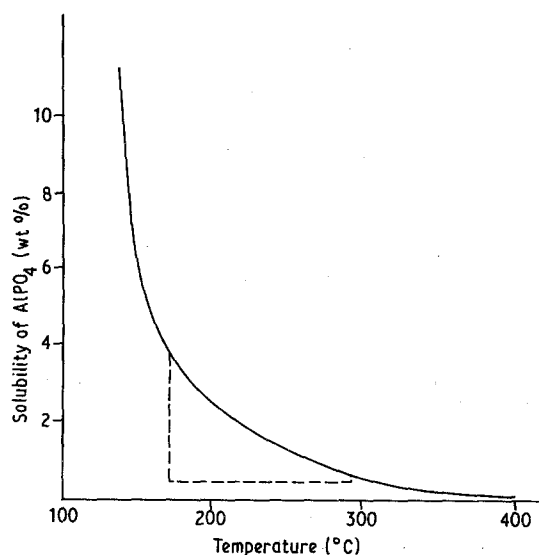


Figure 1 Solubility of AlPO₄ as a function of temperature at a pressure of 2 kp.s.i. in 2 M HCOOH solution.

TABLE III Comparative data of solubility

Solvent	Temperature (° C)	Pressure (kp.s.i.)	Time (days)	Remarks
3 M HCOOH	300	1	5	—
3.05 M NaOH*	170	10	3	Residue no AlPO ₄
2 M NH ₄ Cl	300	1	5	High solubility
4.62 M Na ₃ PO ₄ *	300	10	3	Residue not AlPO ₄
2 M HCOOH	300	1	5	Good solubility
3 M Na ₂ HPO ₄ *	300	10	5	1% solubility
2.5 M NH ₄ Cl	300	1	5	Fairly good solubility
3.05 M CH ₃ COOH*	170	10	3	Negligible solubility
2 M NaHCO ₃	300	1	5	Fairly good solubility
2 M NaCl	300	1	5	Negligible solubility
3.05 M NaCl*	170	10	3	4% solubility
2 M NaF	300	1	5	Good solubility
2 M KF	300	1	5	Good solubility
2 M LiF	300	1	5	Good solubility
3.05 M NH ₄ HF ₂ *	300	10	5	Residue not AlPO ₄
2 M NH ₄ H ₂ PO ₄	300	1	5	Negligible
2 M HCl	300	1	5	Good solubility
3.05 M NF ₄ HF*	170	10	5	Residue not AlPO ₄
3.05 M HNO ₃ *	170	10	5	Negligible solubility
3.05 M NaCl*	300	10	4	Negligible solubility
1 M Na ₂ CO ₃	300	1	5	Negligible solubility

*Reference [8].

the temperature of the furnace should be increased slowly up to the pre-determined temperature. The rate of increase in temperature plays a prominent role in determining the quality of the crystals, rate of crystallization and rate of nucleation. In the case of the solution with higher molarity the rate of growth appeared to be fairly high, particularly in the case of HCl, HCOOH and NaHCO₃.

4. Crystal morphology

The morphology of berlinite crystals varies widely depending upon the growth conditions. The study of the morphology of AlPO₄ is important due to the material's device potential. It is well known that the piezoelectric and dielectric properties depend upon the directions of crystal cuts. With this in mind an attempt has been made to study the morphology of these crystals with reference to

the growth conditions. The crystals obtained, although small in size, exhibit distinct morphological features. The crystal size varies from 0.5 to 3 mm and the common forms are hexagonal, rhombohedral, rod-shaped, needle-like and occasionally rounded. The characteristic photographs of these crystals are shown in Fig. 2. The crystal faces are well developed with highly polished surfaces and exhibit vitreous lustre. The morphological forms mainly depended upon their nutrient composition and the solvent in action [9]. The addition of impurities of divalent and trivalent metals in various proportions produces a distinct variation in colour and morphology. Data for the dependence of the morphological features upon the nutrient composition and the solvent used are given in Table IV.

In experiments carried out with aluminium hydroxide the characteristic morphology was

TABLE IV Morphology of aluminium orthophosphate

Nutrient composition	Temperature (° C)	Morphology
Al ₂ O ₃ + H ₃ PO ₄ mineralizer HCl (1.5 M)	280	Hexagonal and rhombohedral
Al ₂ O ₃ + H ₃ PO ₄ mineralizer NaCl (2 M)	300	Rhombohedral
Al(OH) ₃ + H ₃ PO ₄ mineralizer NaF (2.5 M)	300	Rod-shaped, needle-shaped or ascicular
Al ₂ O ₃ + H ₃ PO ₄ mineralizer NH ₄ Cl (4 M)	300	Small hexagonal, rhombohedral and equi-dimensional
Al ₂ O ₃ + H ₃ PO ₄ mineralizer HCOOH (2 M)	280	Hexagonal and rhombohedral
Al ₂ O ₃ + H ₃ PO ₄ mineralizer NaHCO ₃ (3 M)	300	Hexagonal, rhombohedral and slightly irregular

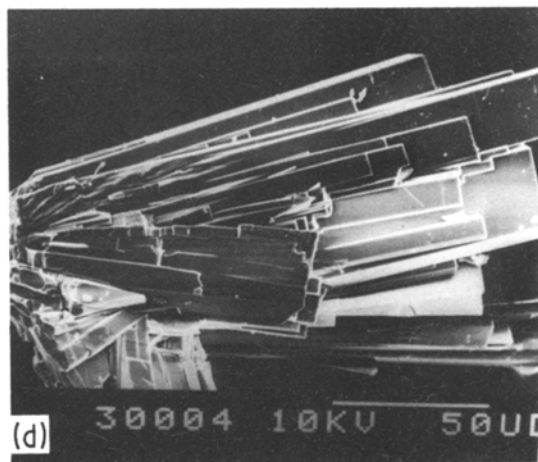
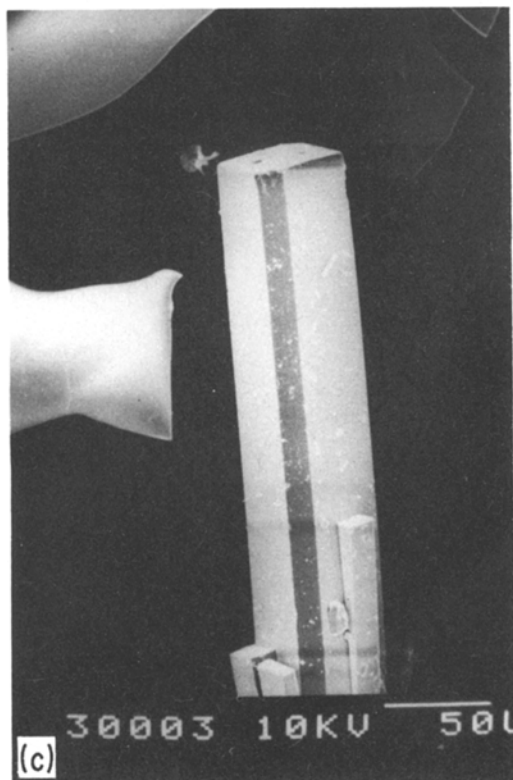
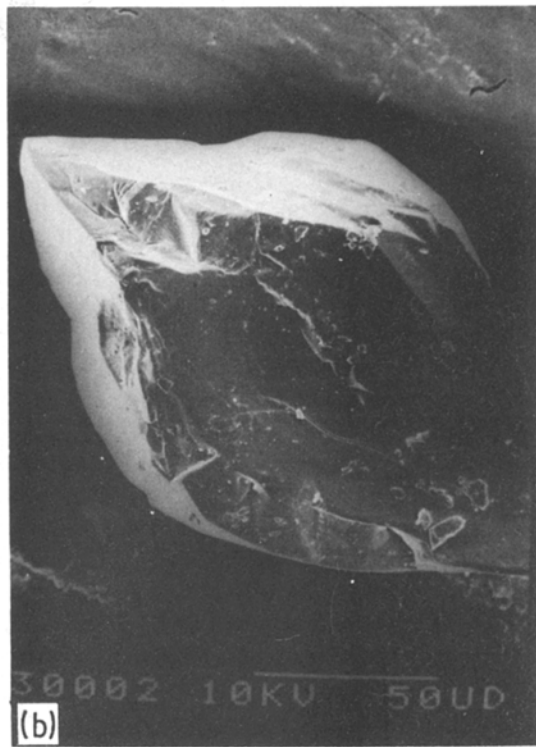
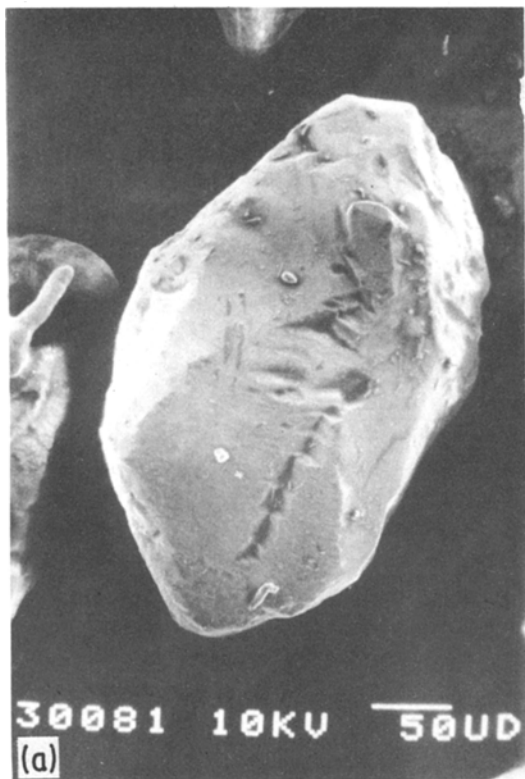


Figure 2 Characteristic appearance of AlPO₄ crystals.

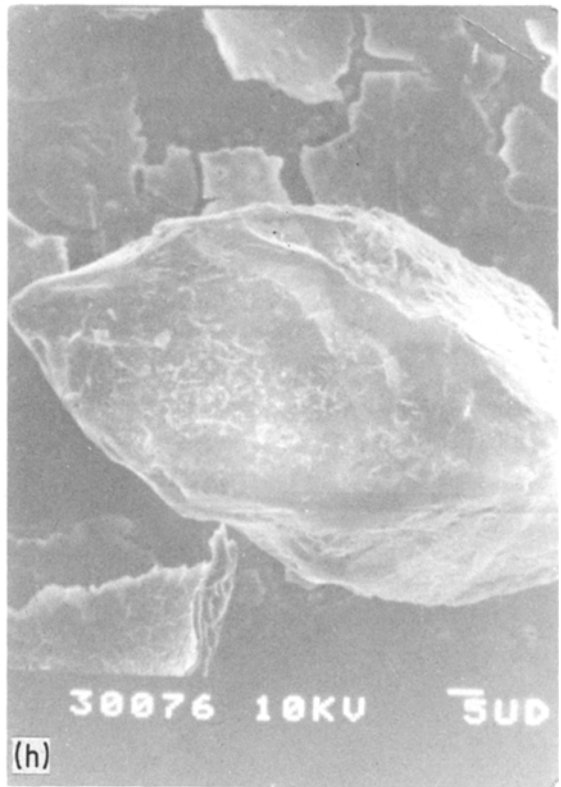
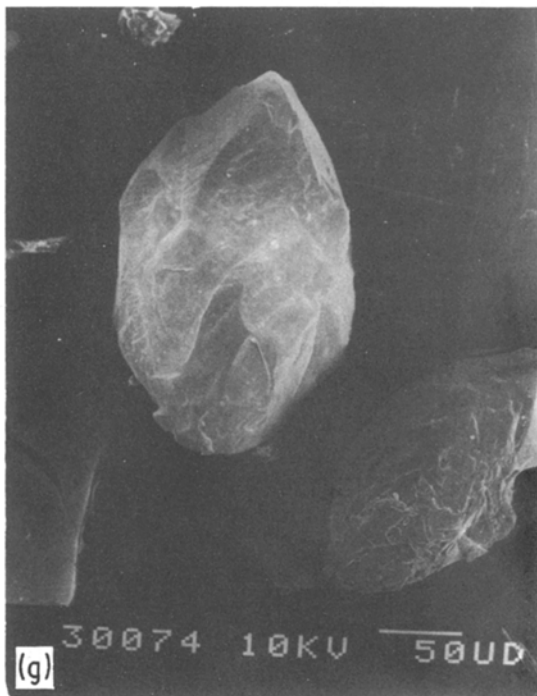
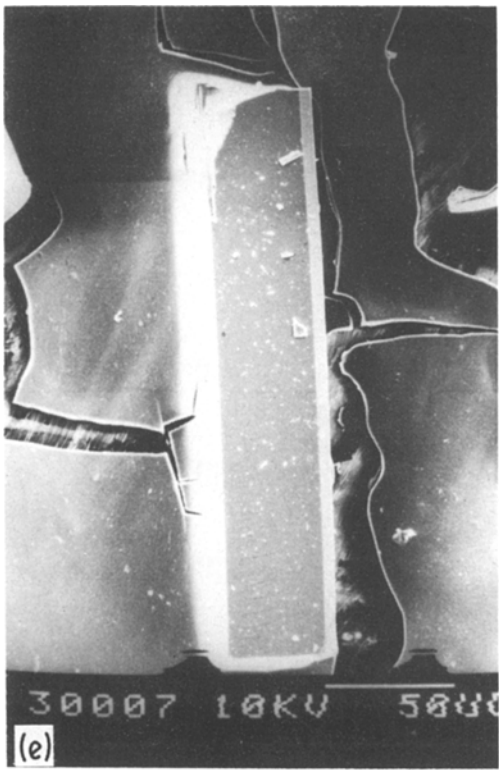


Figure 2 Continued

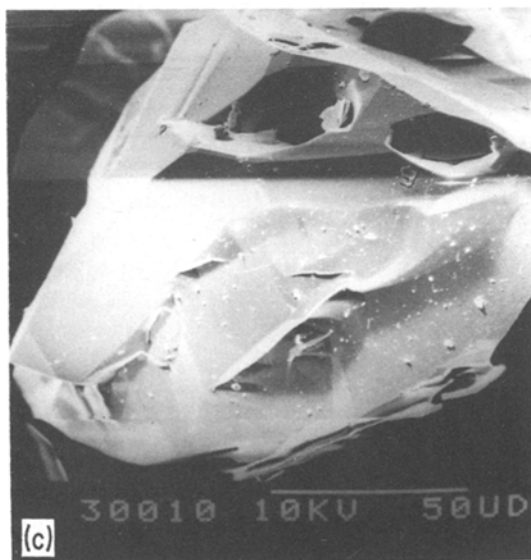
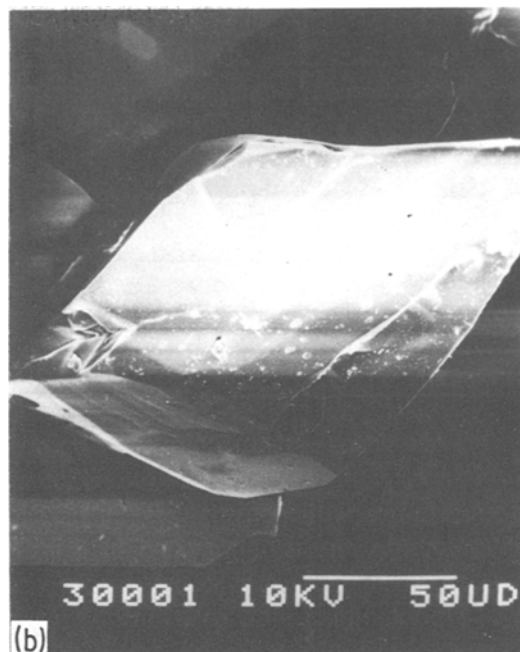
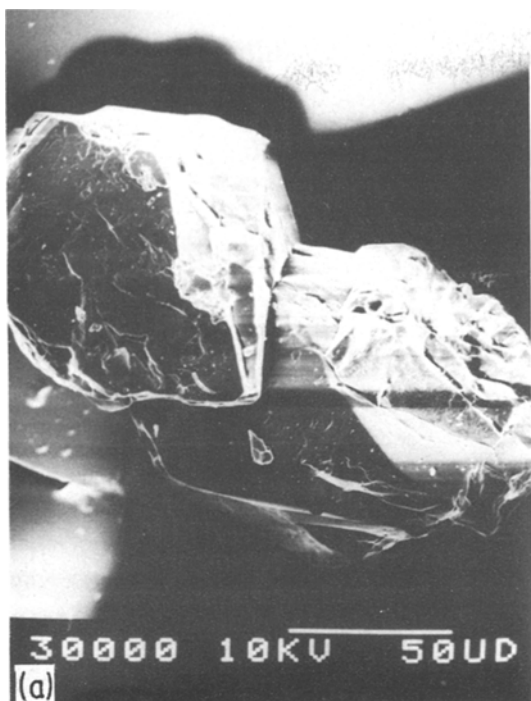


Figure 3 Characteristic appearance of cubic crystals of sodium chloride.

aluminium hydroxide and sodium aluminate the rate of crystallization is higher and also more crystals will develop. In experiments carried out with Al_2O_3 , H_3PO_4 and a high molar NaCl solution, cubic crystals of NaCl are obtained in association with hexagonal berlinite crystals. These crystals dissolve during washing and this occurred in almost all the experiments with a high molar sodium chloride solution. The characteristic appearance of these cubic crystals is shown in Fig. 3.

5. Characterization of berlinite crystals

The crystals obtained were characterized using X-ray diffraction, IR spectroscopy, etc. X-ray powder diffraction and analysis was carried out on all the characteristic samples. Some of the samples were subjected to X-ray irradiation for many hours but no visual effect was observed. In samples doped with various metals, colour changes were noticed after irradiation. IR spectra for berlinite crystals were taken on a Specord spectrophotometer using liquid paraffin in the range 500 to 3800 cm^{-1} . The absorption band for $(\text{OH})^{-1}$ is very distinct and also the absorption coefficient for $(\text{OH})^{-1}$ at $3.1\text{ }\mu\text{m}$ is quite high.

needles or rod-shaped (1 to 3 mm in size), irrespective of either the mineralizer used or the growth temperature. In the case of sodium aluminite, berlinite crystals were needle-like or ascicular. Aluminium oxide gives hexagonal, rhombohedral or equi-dimensional crystals. It is interesting to note that the changes in morphology are mainly due to the variation in the nutrient composition and not due to the variation in the growth temperature, pressure and per cent fill. In case of

The absorption coefficient for $(\text{OH})^{-1}$ influences the dielectric constant of berlinite crystals. A detailed study of IR spectra for berlinite crystals will be reported elsewhere.

6. Conclusions

1. Berlinite single crystals can be grown hydrothermally using teflon liners, which are more effective than the usual platinum liners.

2. NH_4Cl , HCOOH , NaF and KF are the promising new solvents for hydrothermal growth of berlinite crystals and all four show good solubility.

3. Rod-shaped crystals are characteristic in the case of sodium aluminate and finally hexagonal, rhombohedral or equi-dimensional crystals are common in the case of aluminium oxide. The solvent used will play a minor role in the morphology of these crystals.

4. Cubic crystals are noticed before washing in the resultant product of experiments carried out with high molar NaCl solutions as solvent.

5. Almost all the crystals of berlinite grown by a hydrothermal technique contain a distinct amount of water.

Acknowledgements

We would like to thank Professor M. N. Viswanathiah, Vice-Chancellor of the University of Bangalore and Professor K. S. Hedge, Vice-

Chancellor of the University of Mysore, for active encouragement in this work. We would also like to thank Dr Prahallad for SEM photographs and Mr Vidyasagar for IR spectra.

References

1. W. VON JAHN and E. KORDES, *Chem. Erde* 70 (1953) 75.
2. J. M. STANLEY, *Ind. Eng. Chem.* 46 (1954) 1684.
3. D. F. CROXALL, I. R. A. CHRISTIE, B. J. ISHERWOOD, A. G. TODD and J. BIRCH, "The Growth and Assessment of Berlinite Single Crystals", C118, ECCG-2, Sept. 10-15 (1979), Lancaster, England.
4. R. F. BELT and L. E. DRAFALL, "Hydrothermal Growth of Berlinite (AlPO_4)", C119, ECCG-2, Sept. 10-15 (1979), Lancaster, England.
5. E. D. KOLB and R. A. LAUDISE, *J. Crystal Growth* 43 (1978) 313.
6. W. P. MASON, "Piezoelectric Crystals and their Applications to Ultrasonics" (Van Nostrand, New York, 1950) p. 84.
7. K. BYRAPPA and B. N. LITVIN, *J. Mater. Sci.* 18 (1983) 703.
8. E. D. KOLB, J. C. GRENIER and R. A. LAUDISE, *J. Crystal Growth* 51 (1981) 178.
9. K. HASEGAWA, K. MINEGISHI and S. SOMIYA, Abstracts for the International Symposium on Hydrothermal Reactions, No. 89, Tokyo Institute of Technology, Yokohama, Japan, March 22-26, 1982.

Received 26 September
and accepted 3 November 1983