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Influence of admixtures on the crystallization and morphology of $AlPO_4$ crystals

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The influence of various uni-, bi-, tri- and tetravalent admixtures on the crystallization and morphology of $AlPO_4$ has been studied in detail. $AlPO_4$ crystals were synthesized under hydrothermal conditions. It was found that the phase formation and morphology vary with the type of admixture and its concentration. The crystals were hexagonal, rhombohedral, rounded, irregular, rod shaped and massive in habit. With an increase in the concentration of admixtures, two phases (berlinite and metaphosphates) of the respective admixtures crystallize simultaneously.

1. Introduction

$AlPO_4$ is being studied extensively as an important substitute for the traditional piezo-electric quartz. This $AlPO_4$ (berlinite) has better piezo-electric effects than α-quartz and has the greatest prospects in electronic industries. Although the first report on the growth of $AlPO_4$ appeared somewhere in the early fifties, the study of this material became popular only in the latter part of the seventies [1–5]. Perhaps the best known reasons may be the problems connected with the negative temperature coefficient of solubility, the lack of data on phase equilibria in the respective phosphate systems, lack of growth technology in the phosphorus media and so on. Even today, materials scientists are yet to conquer the problems of reproducibility, perfection and growth rates. As Laudise *et al.* correctly point out, our understanding of $AlPO_4$ is comparable to that of quartz 25 years ago [6]. In the literature available on $AlPO_4$, quite a lot of work has been done on the synthesis, types of solvents, solubility, *P–V–T* behaviour in some systems and so on, but little work has been done on the actual growth and characterization. Study of the growth is still with reference to the presence of various admixtures, selected doping and the characterization, particularly the piezo-electric constants. It is predicted that the use of dopants or admixtures might further improve the piezo-electric effect of $AlPO_4$, in some cases new opto-electronic materials ($AlPO_4$ crystals doped with active ions such as neodymium, europium, etc.), very high temperature ceramics and so on, may be obtained. With this aim the present authors have made an attempt to use some admixtures in the crystallization of $AlPO_4$ and studied the influence of these admixtures on the crystallization, growth rate, morphology, internal structures, the thermal behaviour and so on. The changes in the internal structures and the thermal behaviour have been recorded through infrared spectroscopy and differential thermal analysis, which will be published separately. The present report has been limited to the study of influence of admixtures on the crystallization and morphology of $AlPO_4$.

2. Experimental method

The most popular method of growing $AlPO_4$ (hydrothermal method) has been employed in the present work. A detailed report on the crystallization of $AlPO_4$ has been given in the earlier report [7]. The experiments were carried out for 8 days at 250° C using teflon liners in Morey-type autoclaves of capacity 25 to 50 ml. Since the crystallization occurred due to spontaneous nucleation, the temperature of the furnace was slowly increased to control the rate of nucleation (nearly $5° C h^{-1}$). Over 100 experiments were conducted with different starting materials in different proportions and finally an ideal experiment was selected for adding the admixtures. This ideal experiment can be written as follows:

$AlCl_3$,	3 g
H_3PO_4 (85%),	5 ml
HCl (2 M),	3.5 ml
Temperature,	250° C
Pressure,	100 atm
Duration,	8 days.

Various admixtures were introduced into this ideal experiment. All the admixtures can be grouped into univalent, bivalent, trivalent and tetravalent types. In most cases these admixtures were introduced in the form of gels of respective elements and in some cases they were taken as oxides or hydroxides. The following admixtures have been considered in the present report:

Univalent	potassium, rubidium
Bivalent:	magnesium, barium, beryllium, lead, copper, nickel, zinc

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TABLE I Results of the chemical analysis for $AlPO_4$ crystals*

No.	Admixture	Al_2O_3 (wt %)	P_2O_5 (wt %)	Concentration of admixture
1	K	49.79	50.08	240 p.p.m.
2	Rb	40.32	59.58	40 p.p.m.
3	Mg	44.68	54.85	176 p.p.m.
4	Pb	47.54	52.11	365 p.p.m.
5	Be	40.37	59.52	135 p.p.m.
6	Cu	45.81	54.07	117 p.p.m.
7	Fe	48.41	51.39	186 p.p.m.
8	Cr	41.67	58.31	410 p.p.m.

*The starting concentration of admixtures was 1.5 wt % in all cases.

Trivalent: iron, chromium, bismuth, lanthanum, cerium, neodymium, gadolinium

and

Tetravalent: zirconium, titanium.

It was found that these admixtures play an important role in the process of crystallization and morphology of $AlPO_4$.

3. Discussion

Chemical analysis of the representative samples of berlinite crystals containing various admixtures was carried out. Two series of experiments have been conducted. The starting concentration of admixtures in the first series of experiments was kept at 1.5 wt % and in the second series of experiments at 4 wt %. However, in the resultant products, the concentration of admixtures reduced considerably, but they did influence the crystallization processes, morphology and a host of other features. The exact concentration of these admixtures in the resultant products was determined by wet chemical analysis using atomic absorption spectrophotometry (Model IL-751 AAS-AES, USA) to the p.p.m. and p.p.b. level. The results of the chemical analysis are given in Table I.

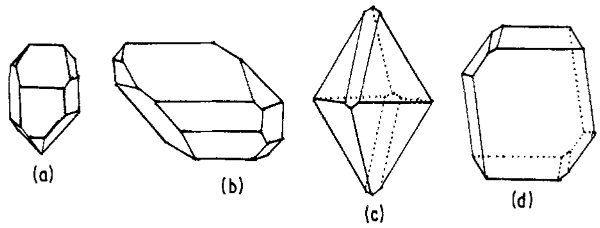

Figure 1 Distorted forms of quartz (a & b) and lazulite (c & d) [9].

As stated earlier, these admixtures influence the crystallization processes and the morphology. Table II gives the type of admixtures and their effects on various parameters such as colour, lustre, size and morphology. From Table II, it is evident that there is a wide variation in the morphology of berlinite crystals. In the actual experiments without any admixtures, well developed rhombohedral and hexagonal crystals were observed, but with the addition of various admixtures the crystals change to fibrous, rod shaped, acicular, massive, equi-dimensional and irregular shapes. In the case of zirconium and titanium, fibrous or acicular crystals were obtained. Hitherto, such acicular crystals of berlinite were obtained only in experiments containing $Al(OH)_3$ as the starting component [7, 8]. The overall quality of the crystals remained good in most of the cases except in one or two. Twinning in $AlPO_4$ is common in the case of neodymium admixture. With an addition of gadolinium or lead as admixture, there is a sharp increase in the size of the crystals by retaining good quality and morphology. The variation in the forms of $AlPO_4$ with an introduction of admixtures corresponds to the variation in the forms of natural minerals: quartz (SiO_2) and lazulite ($2\ AlPO_4 \cdot (Fe, Mg)(OH)_2$), as shown in Fig. 1 [9]. The characteristic appearance

TABLE II Influence of admixtures on $AlPO_4$ crystals

No.	Admixture	Concentration of admixture (wt %)	Colour transparency lustre	No. of phases	Morphology
1	K	1.5	colourless transparent vitreous	1	rhombohedral, rectangular, equidimensional
		4.0	colourless transparent vitreous	2	small equidimensional
2	Rb	1.5	colourless transparent vitreous	1	rhombohedral, rectangular
		4.0	colourless subtransparent subvitreous	2	small acicular
3	Cu	1.5	colourless transparent vitreous	1	somewhat larger rhombohedral
		4.0	colourless transparent vitreous	1	small rhombohedral
4	Mg	1.5	colourless vitreous transparent	1	rhombohedral, *c*-axis extended more
		4.0	buff white subtransparent subvitreous	2	twinned rhombohedral

TABLE II *Cont.*

No.	Admixture	Concentration of admixture (wt %)	Colour transparency lustre	No. of phases	Morphology
5	Pb	1.5	colourless transparent vitreous	1	big rhombohedral, *b*-axis also slightly extended
		4.0	buff white subtransparent subvitreous	2	very small equidimensional
6	Ni	1.5	white subtransparent subvitreous	2	rectangular, thin rectangular
		4.0	No crystallization of a stable phase		
7	Co	1.5	light pink subtransparent subvitreous	1	fine grained crystalline powder
8	Ba	1.5	white subtransparent subvitreous	1	small rounded polycrystalline
		4.0	white subtransparent subvitreous	1	small rounded polycrystalline
9	Be	1.5	colourless transparent vitreous	1	rhombohedral
10	Fe	1.5	colourless transparent vitreous	1	rhombohedral, equidimensional, trigonal
		4.0	colourless transparent vitreous	2	rectangular, equidimensional
11	Cr	1.5	light green transparent vitreous	1	rhombohedral, hexagonal
		4.0	light green transparent vitreous	2	small irregular
12	Bi	1.5	colourless transparent vitreous	1	needles, triangular
		4.0	colourless transparent vitreous	2	needles, triangular
13	La	1.5	white transparent vitreous	1	rhombohedral, massive
		4.0	white subtransparent subvitreous	1	very fine grained crystalline powder
14	Ce	1.5	white subtransparent subvitreous	1	small acicular
15	Nd	1.5	colourless transparent vitreous	1	intertwinned rhombohedral
16	Zn	1.5	white subvitreous subtransparent	1	small equidimensional
17	Zr	1.5	white subtransparent subvitreous	1	small acicular
		4.0	white subtransparent subvitreous	1	small equidimensional
18	Ti	1.5	white subtransparent subvitreous	1	small acicular
		4.0	white subtransparent subvitreous	2	small acicular

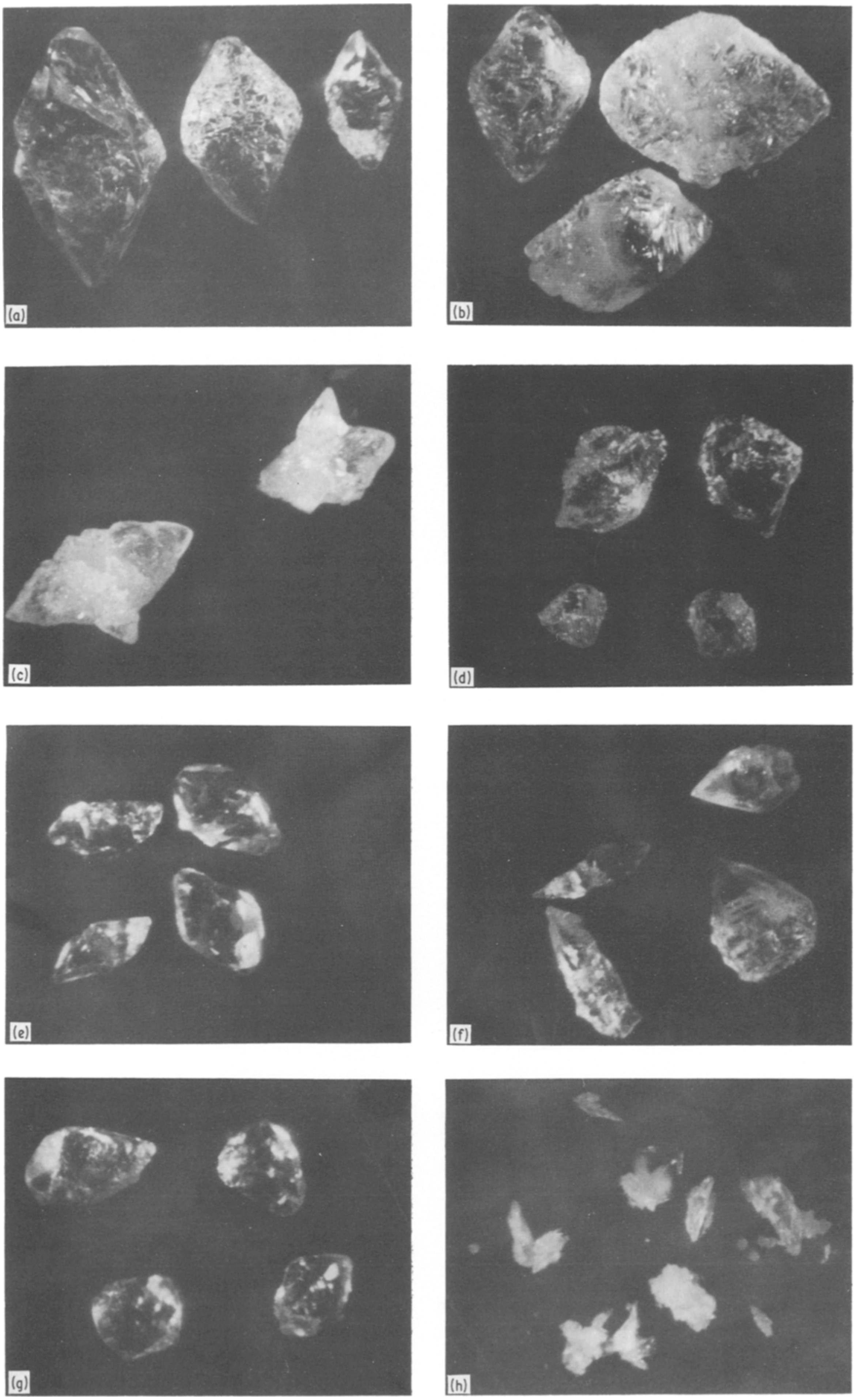

Figure 2 Characteristic photographs of $AlPO_4$ crystals containing various admixtures: (a) without admixture, × 35; (b) with lead, × 16; (c) with neodymium, × 19.6; (d) with potassium, × 21; (e) with magnesium, × 14; (f) with bismuth, × 14; (g) with iron, × 14; (h) with zinc, × 10.5; (i) with barium, × 14.

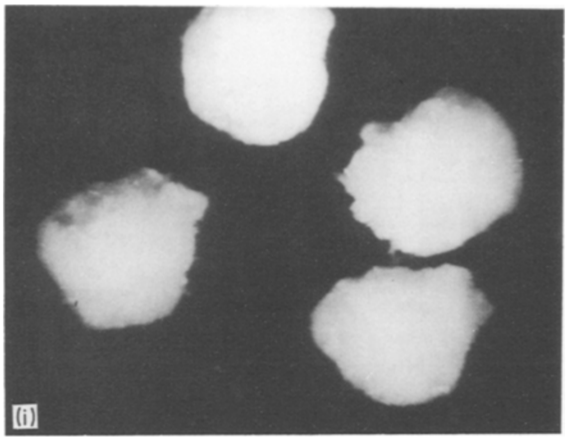

Figure 2 continued.

of berlinite crystals containing various admixtures is shown in Fig. 2. With an increase in the concentration of admixtures (experiments with 4 to 5 wt % admixtures), the quality of $AlPO_4$ crystals reduces to a greater extent, in some cases it leads to the formation of two separate phases such as $AlPO_4$ and the *ortho*- or *meta*-phosphate of the respective admixture, and also in some cases the crystallization of a stable phase ceases. Therefore, it can be predicted that the structure of $AlPO_4$ is quite strong (similar to quartz) and these admixtures cannot diffuse strong Al–O and P–O bonds and this leads to the formation of two separate phases. Since, the concentration of these admixtures is quite small (Table I), it shows that these admixtures go only as interstitial ones and not as substitutional ones.

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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, L. R. A. CHRISTIE, B. J. ISHERWOOD, A. G. TOOD and J. BIRCH, "The Growth and Assessment of Berlinite Single Crystals", C118, ECCG-2, 10–15 September (1979), Lancaster, UK.
4. R. F. BELT and L. E. DRAFALL, "Hydrothermal Growth of Berlinite ($AlPO_4$)", C119, ECCG-2, 10–15 September, Lancaster, UK.
5. E. D. KOLB and R. A. LAUDISE, *J. Cryst. Growth* **43** (1978) 313.
6. R. A. LAUDISE, E. D. KOLB and P. L. KEY, In "Hydrothermal Synthesis and Crystal Growth-History, Status and Prospects", Proceedings of the International Symposium on Hydrothermal Reactions, Tokyo Institute of Technology, Yokohama, Japan, 22–26 March (1982).
7. K. BYRAPPA, A. VENKATACHALAPATHY and B. PUTTARAJ, *J. Mater. Sci.* **19** (1984) 2855.
8. K. HASEGAWA, K. MINEGISHI and S. SOMIYA, Abstracts for the International Symposium on Hydrothermal Reactions, No. 89, Tokyo Institute of Technology, Yokohama, Japan, 22–26 March (1982).
9. E. S. DANA, "A Textbook of Mineralogy" (Wiley, New York, 1955) p. 196.

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