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## Hydrothermal growth of OH-free $\text{AlPO}_4$ and $\text{GaPO}_4$ crystals, the way of twin reducing

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**ABSTRACT :** Water-free crystals of  $\text{AlPO}_4$  and  $\text{GaPO}_4$  have been grown in the temperature region 350-500°C by the direct temperature gradient technique under hydrothermal conditions. The concentrated solution of phosphoric acid with boiling temperature 225-240°C has been used as solvent. The characteristic features of twins in the crystals have been found and explained. The investigations of growth kinetics the specific features of twinning and growth mechanism have resulted in the choice of the seeds with special shape, size and orientation for growing crystals with lower quantity of twins and dislocations.

### 1 - INTRODUCTION

Berlinite ( $\text{AlPO}_4$ ) and  $\text{GaPO}_4$  crystals are quartz isomorphs. They belong to the trigonal symmetry, space group is  $P3_12$  or  $P3_22$ . Alternation of  $\text{Al}^{3+}$  ( $\text{Ga}^{3+}$ )- and  $\text{P}^{5+}$  in the positions of  $\text{Si}^{4+}$  atoms explains the doubling of the lattice parameter  $c$  as compared with quartz. The presence of screw axes  $3_1$  and  $3_2$  leads to the appearance of the structures with right and left rotation. The enantiomorphic structures form the twins with parallel axes due to the regular growing each other.

The presence of twins in the Al- and Ga-orthophosphates is the main cause of piezoelectric property deterioration.

The synthesis of berlinite and  $\text{GaPO}_4$  crystals has been usually carried out by the hydrothermal technique (at  $T < 250^\circ\text{C}$ ) [1-6] ; the reverse temperature gradient or slow temperature increasing has been used ; different acids, i.e.  $\text{H}_3\text{PO}_4$  [1-4],  $\text{HCl}$  [5],  $\text{HCOOH}$  [6] have been served as solvents. The crystals grown at the  $T < 250^\circ\text{C}$  contain OH-groups.

The water presence is the second cause of piezoelectric property deterioration in Al and Ga-orthophosphate crystals.

Nowadays, only berlinite and Ga-orthophosphate obtained in sulfuric acid have a low OH-content [7].

This paper describes the method of growing OH-free  $\text{AlPO}_4$  and  $\text{GaPO}_4$  crystals and the possible way of twin reducing.

### 2 - EXPERIMENT

The temperature region (350-500°C) with the positive temperature coefficient of Al and Ga orthophosphates solubility has been chosen for crystal growth. The direct temperature gradient at vertical position of Pt - lined autoclaves was employed [8].

To avoid the water entrance in the crystals, the concentrated phosphoric acid solution with boiling temperature 225-240°C was used as a solvent. Practically, there is no water in such solvent and it consists of orthophosphoric acid (90 %) and pyro-phosphoric acid (10 %). The solution was presaturated with  $\text{AlPO}_4$  or  $\text{GaPO}_4$  to avoid the dissolution of the seeds.

To prevent the solution boiling during the crystal growth, the inert gas was pumped into an autoclave up to 50 bars.

Crystals obtained have been studied by IR-spectroscopy, etching method, X-ray topography.

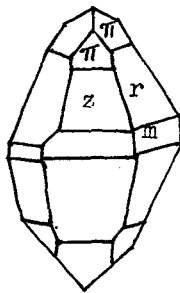
### 3 - RESULTS

The crystals obtained by this method have the length along c-axis up to 50 mm for  $\text{AlPO}_4$  and about 40 mm for  $\text{GaPO}_4$ .

IR-spectroscopy data of the crystals grown under such conditions has confirmed the absence of OH-groups [9].

#### 3.1 - Crystal habit

The typical habit of  $\text{AlPO}_4$  and  $\text{GaPO}_4$  crystals is given in Fig. 1.



$r\{10.1\}$   
 $z\{01.1\}$   
 $m\{10.1\}$   
 $\pi\{10.2\}$   
 $\pi'\{01.2\}$

Table 1 : Values of growth rates.

T°C	350	375	400	425
$V_{\pi'}$ {01.2}	0,14	0,20	0,65	
$V_{\pi}$ {10.2}	0,07	0,19	0,25	0,30
$V_m$ {10.0}	0,10	0,14	0,32	0,53
$V_z$ {01.1}	0,13	0,20	0,26	0,33
$V_r$ {10.1}	0,06	0,13	0,15	0,18

Figure 1 : The typical habit.

The faces  $r$ ,  $\pi$  and  $z$  prevail in the crystal grown at high temperature ( $> 400^\circ\text{C}$ ). With the temperature decreasing the growth rates of faces decrease and the crystal habit become more isometric. The faces  $m$  and  $\pi'$  appear in the crystal habit below  $400^\circ\text{C}$ . At  $T > 400^\circ\text{C}$  the skeleton growth occurs on these faces. The growth rates along various crystallographic directions decrease in the following sequence :

$$V_z(0001) \gg V_{\pi'}(01.2) > V_m(10.0) > V_z(01.1) > V_{\pi}(10.2) > V_r(10.1)$$

The value of growth rates for equilibrium faces at different temperature are given in table 1.

In contrast to crystals grown by low-temperature techniques, berlinite and Ga- orthophosphates grown under high temperature have not the pinacoid as equilibrium face. On the seed with (0001) orientation the skeleton growth takes place at  $T > 350^\circ\text{C}$ . The mechanism of skeleton growth will be described below.

#### 3.2 - Twinning

The growth twins according to the Dauphiné, Brazil and Leydolt's twinning laws have been found both in  $\text{AlPO}_4$  and  $\text{GaPO}_4$  crystals [10, 11].

On the basic  $r$  and  $z$  rhombohedra, the etch pits with typical shape and orientation have been observed. The etching of crystal faces occurs during the autoclave cooling in the region of retrograde solubility.

The etch pits on rhombohedra of  $\text{AlPO}_4$  and  $\text{GaPO}_4$  crystals look similar each other (Figure 2a). Their analysis allows to distinguish the right and the left rotated crystals. These data and the shape of twin boundaries allow to find the twinning law.

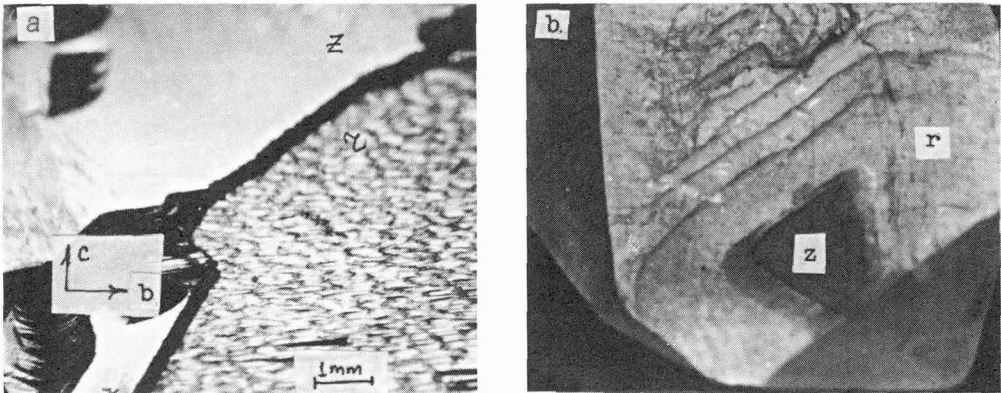


Figure 2 : Right Dauphiné twin in berlinite (a) ; Dauphiné twin in GaPO<sub>4</sub> (b, x 4).

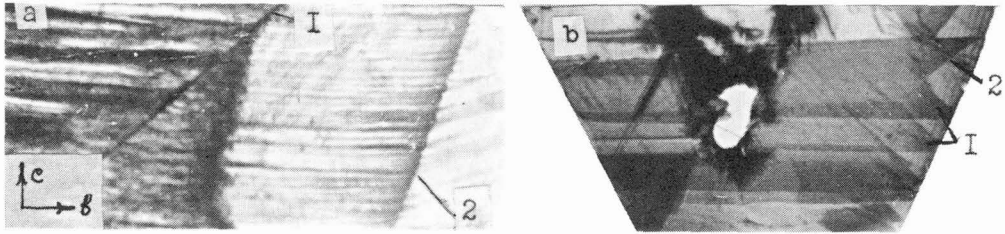


Figure 3 : Brazil twin boundaries with two orientations. (a) on the rhombohedra ; (b) on (0001) plane (X-ray pattern). 1 - plane  $\pi\{10.2\}$  ; 2 - plane  $\pi'\{01.2\}$ .

The Dauphiné twins in GaPO<sub>4</sub> have somewhat different morphology in comparison with berlinite due to larger difference between the growth rates of the r- and z-faces in these crystals. The part represented by faster growing z-rhombohedron is located upper than r-rhombohedron (Figure 2b).

The Brazil twins in our crystals have been observed more often. The boundaries of Brazil twins look like the straight lines dividing the regions with the same indices, but with the opposite rotation.

The Brazil twins in berlinite have some characteristic features in comparison with quartz and Ga-orthophosphate.

In berlinite, on the basic rhombohedra r and z, the Brazil twin boundaries with two orientations have been found (Figure 3a).

Two planes with different indices can be easily seen on the X-ray topography patterns of the pinacoid plane (Figure 3b). This picture has shown the twin planes with two different orientations, corresponding to the rhombohedra of both indices :  $\pi\{10.2\}$  and  $\pi'\{01.2\}$ .

### 3.3 - The growth mechanism on pinacoid

Crystal growth on the pinacoidal seed takes place by the following mechanism. The "poly-head" growth occurs on the whole surface of the (0001) seed. Each head is formed by the r and z faces (Figure 4a).

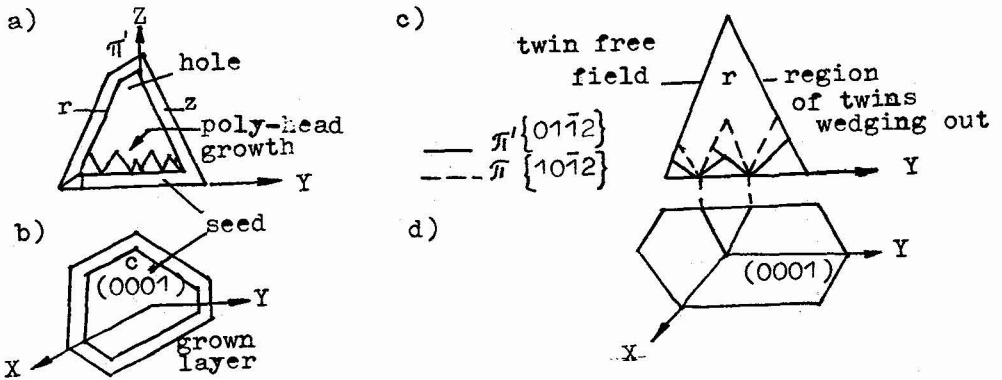


Figure 4 : The ZY (a) and XY (b) cross section of grown crystal ; wedging out the twins on the r-rhombohedron (c) ; twin on pinacoid (d).

From the lateral surfaces of the pinacoidal seed the skeleton growth of r and z rhombohedra begins. The rhombohedra have the high tangential rates and the formation of such skeleton framework (built by equilibrium rhombohedra) occurs very quickly. Usually the inner part of equilibrium framework is filled with the solution.

The faces r and z forming the hollow framework are characterized by a good quality. Brazil twin boundaries are wedged out in the narrow region close to the seed (Figure 4c). The upper part of the rhombohedra is free from twins and dislocations.

3.4 - The way of twin reducing

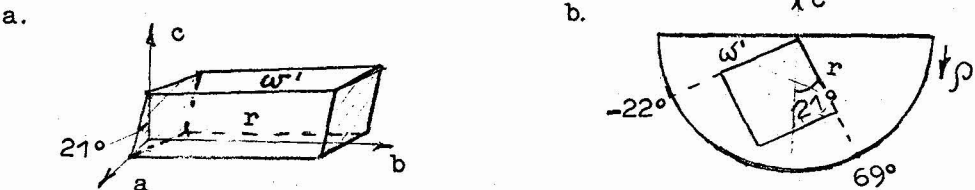


Figure 5 : Orientation of bar-seed (a). Cross-section of the bar (b).

The investigation of the growth kinetics, characteristic features of twinning and growth mechanism allows to choose the seed with optimum shape, size and orientation for crystal growth. Such seed looks like it is shown in figure 5a. It is the bar with a square section, cut along b-axis. One face of the bar is presented by r-rhombohedron. The other is  $\omega'$ -rhombohedron bar's length defines the final crystal size along c-axis because the tangential growth rate of r-face is rather high and the crystal regeneration occurs very quickly in this direction. The bar has the narrow width in order to reduce the quantity of the inherited defects. The twins wedging out occurs in the narrow region close to the seed as it was shown earlier.

Crystals grown on such bar-seeds have the lowest quantity of the defects (Figure 6). The wedging out of twin boundaries occurs in the narrow region close to the seed as it was shown for pinacoidal seed.

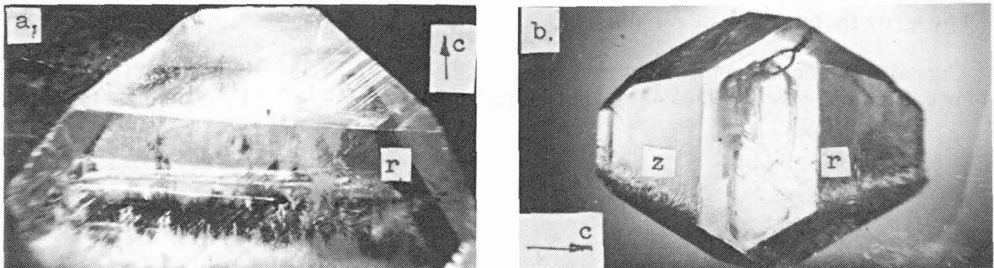


Figure 6 : Berlinites crystal grown on the bar-seed. (a) - crystal habit (x 2) ; (b) - reducing the twins in the upper part of crystal (x 4).

Growth the crystals on such seeds is the possible way of twins reducing.

#### 4 - DISCUSSION

The theoretical boundaries of Brazil twins for r and R-rhomboheda in quartz have been built by Mc.Laren and Phakey [12]. The values of Si-O-Si angles are different for r- and R-boundaries.

The Si-O-Si angle on r-boundary is much less than in the bulky crystal and therefore this boundary will be very strained and such boundary cannot exist in quartz [13].

Usually only Brazil twins with R{10.1} boundary have been found in natural and synthetic quartz and amethyst [14].

In berlinite crystals grown at 500°C, the Brazil twins with boundaries along two planes  $\pi$  and  $\pi'$  have been found due to the fact that crystal growth occurs at the temperature close to the temperature of  $\alpha$ - $\beta$  transition.

This phase transition results in the rising of crystal symmetry up to 6/mm and  $\pi$  and  $\pi'$  rhombohedra are transformed into the hexagonal pyramids.

The change of the O-Al-O angle in  $\text{AlO}_4$  and O-P-O in  $\text{PO}_4$  tetrahedra is very essential in berlinite at 500°C [15]. This change leads to the changing of Al-O-P angle. The structure of rhombohedron becomes closer to hexagonal pyramids. The value of boundary angles on the different Brazil boundaries along  $\pi$  and  $\pi'$  - rhombohedra becomes closer to the angle value in bulky crystal. The appearance of Brazil twins with  $\pi'$ - as well as with  $\pi$ -boundary have the same probability.

There are no change of angle in tetrahedra in  $\text{GaPO}_4$  at 500°C [16], because the inversion between the quartz and cristobalite polymorphs in  $\text{GaPO}_4$  takes place at  $T = 933 \pm 4^\circ\text{C}$  [17]. There are no structure changes in quartz and berlinite when their growth occurs at  $T < 300^\circ\text{C}$ .

That is why the boundaries of Brazil twins along only r{01.1} in quartz, along  $\pi'$ {01.2} in  $\text{GaPO}_4$  and in berlinite grown at  $T < 300^\circ\text{C}$  have not been observed.

#### 5 - CONCLUSION

Water-free  $\text{AlPO}_4$  and  $\text{GaPO}_4$  crystals have been grown by the direct temperature gradient technique at the  $T > 300^\circ\text{C}$ . The concentrated phosphoric acid with boiling  $T = 225\text{-}240^\circ\text{C}$  has been used as solvent.

The specific features of the growth mechanism on pinacoidal seed in high temperature region ( $T > 350^\circ\text{C}$ ) have been described. The wedging out of Brazil twin boundaries in the narrow part close to the seed have been noticed.

Twinning in berlinite and  $\text{GaPO}_4$  have been studied. It is shown that Brazil twin boundary along  $\pi'$ -rhomboheda does not exist in  $\text{GaPO}_4$  and in quartz but it has been found in berlinite. The comparative analysis of Brazil twins in  $\text{SiO}_2$ ,  $\text{AlPO}_4$  and  $\text{GaPO}_4$  allows to explain such boundary existence in berlinite grown at 500°C and its absence in  $\text{GaPO}_4$  and in natural and synthetic quartz and amethyst.

The investigation carried out leads to the choice of the seed with optimum shape, size and orientation. For the crystals grown on such type of seed, a visible reducing of Brazil twins and dislocations is observed.

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