

Growth of gallium orthophosphate single crystals in acidic hydrothermal solutions

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The hydrothermal growth of GaPO₄ single crystals has been studied in several solutions. Among many solutions, H₃PO₄, HCl and H₂SO₄ solutions were found to be effective solvents for the growth of GaPO₄ single crystals. Single crystals have been hydrothermally grown at temperatures over the range 210 to 290 °C in these solutions with seed crystals. HCl solution was found to be the most effective solvent in which to grow large single crystals. Morphologies of crystals grown at temperatures below 200 °C tended to be bounded by small major rhombohedral (1 0 $\bar{1}$ 1) faces. In the temperature range from 210 to 430 °C, the crystals have morphologies bounded by prism (1 0 $\bar{1}$ 0), small major rhombohedral (1 0 $\bar{1}$ 1) and minor rhombohedral (0 1 $\bar{1}$ 1) faces, and grew with well developed basal (0 0 0 1) faces with increase in the growth temperature. Single crystals of GaPO₄ with lower dislocation density have been hydrothermally grown at 210 to 290 °C in 3 M H₃PO₄ solution.

1. Introduction

The low temperature (α) quartz type of AlPO₄ and GaPO₄ single crystals have been known to have similar modifications to SiO₂ [1]. It is well known that the single crystal of AlPO₄ has a similar structure to GaPO₄ single crystal and a piezoelectric coupling constant larger than that of α -quartz [2, 3]. In this respect, AlPO₄ and GaPO₄ single crystals are probably favourable for the device applications.

The α forms of AlPO₄ and GaPO₄ single crystals are stable below 584 and 976 °C, respectively, and suffer a phase transition and the decomposition [4–8]. This fact suggests that the hydrothermal growth method is appropriate for growing these single crystals. Most of the growth methods now used are based on the vertical reverse temperature gradient method employed by Stanley [9] and the horizontal temperature gradient method proposed by Krau and Lehmann [2], where the single crystals have been hydrothermally grown by slow heating of the saturated solution in an autoclave. The growths of AlPO₄ and GaPO₄ single crystals are usually difficult due to their negative temperature coefficient of solubility. In the past few years, the crystal growth of AlPO₄ and the feasibility of large crystals have been much studied. Kolb *et al.* [10] showed that the AlPO₄ single crystals could be grown at rate of a few mm per day when hydrochloric acid is used as a solvent. In addition, a modification of the growth method and morphology of AlPO₄ single crystals have been reported [11–13].

In most studies, GaPO₄ single crystals have been hydrothermally grown at temperatures below 300 °C in phosphoric acid solution [6–8, 14–17]. Detailed data on the crystal growth of GaPO₄ have not, however, been available in hydrothermal acid solution. This paper describes the hydrothermal growth condi-

tion and the morphology of GaPO₄ single crystals in hydrothermal acid solutions.

2. Experimental procedure

Synthesis of the starting powders using a stoichiometric mixture of Ga₂O₃ and NH₄H₂PO₄ has already been reported [6–8], and was carried out with a commercial GaPO₄·5H₂O in the present work. The selection of the effective solvents was performed by the preliminary solubility measurement using the weight loss method as [6–8] and the phase stability after a run. Typical vessels made of silica, pyrex glass or gold were used for the hydrothermal treatments and crystal growth of GaPO₄. Growth runs of GaPO₄ single crystals were carried out by the vertical reverse temperature gradient method and the horizontal temperature gradient at temperatures below 430 °C in several solutions. A modified technique was also used, that is the combination of increasing temperature of the vessel with the vertical reverse temperature gradient.

The grown crystals were characterized by Fourier transform – infrared (FT-IR) spectroscopy. The growth rates and morphologies of the grown crystals were observed by optical microscopy. Dislocation densities of the grown crystals were examined by the etching technique. The grown crystals were etched for 3 min in concentrated boiling H₃PO₄. Etch pits on a crystal surface were investigated by the optical microscopy.

3. Results and discussion

3.1. Synthesis of the starting powders

The starting powders of GaPO₄ were prepared by the hydrothermal treatment of a commercial GaPO₄.

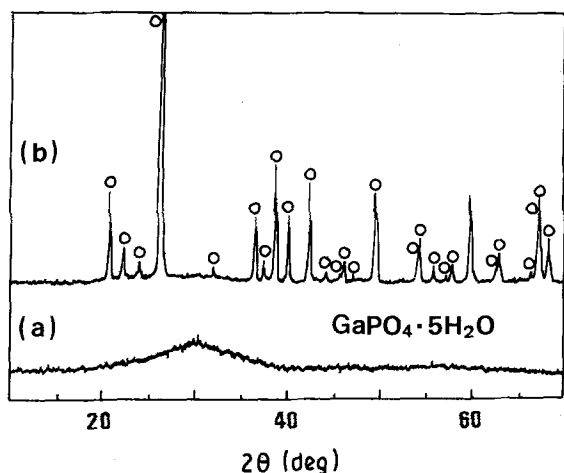


Figure 1 X-ray $\text{CuK}\alpha$ diffraction profiles, (a) $\text{GaPO}_4 \cdot 5\text{H}_2\text{O}$ and (b) hydrothermally treated at 170°C for 3 days in $3\text{ M H}_3\text{PO}_4$ solution (\circ GaPO_4).

$5\text{H}_2\text{O}$ at 170°C for 3 days in $3\text{ M H}_3\text{PO}_4$ solution. As shown in Fig. 1b, the synthesized particles were confirmed to consist of the low temperature type of GaPO_4 formed as a single phase. These single phase GaPO_4 particles were used for the solubility measurement and crystal growth.

3.2. Selection of the hydrothermal solvent

The selection of the effective solvents was carried out by the hydrothermal treatment under several conditions. The preliminary solubility measurements indicated that solubilities of GaPO_4 in neutral (e.g. NaCl , KCl) and weak acidic salt (e.g. $\text{NH}_4\text{H}_2\text{PO}_4$, NH_4Cl) are very small compared with H_3PO_4 solution. Solubilities in the strong acids such as HCl and H_2SO_4 solutions were, however, greater than that in H_3PO_4 solution, in which GaPO_4 was the stable phase. The

temperature coefficients of solubility in these solutions were also negative over the range 150 to 300°C . From the above results, H_3PO_4 , HCl and H_2SO_4 solutions were determined as the most promising solvent for the crystal growth of GaPO_4 .

In order to select the concentration of these solvents, the preliminary growth experiments were carried out under the following hydrothermal conditions: temperature, 150 to 300°C ; duration, 3 to 7 days; concentration of solvent, 1 to 4 M . The results showed that the growths of seed crystals in several solutions above 3 M were relatively practical. Consequently, $3\text{ M H}_3\text{PO}_4$, 3 M HCl and $3\text{ M H}_2\text{SO}_4$ solutions were chosen as the hydrothermal solvents for the crystal growth of GaPO_4 .

Fig. 2 shows the FT-IR spectra of GaPO_4 single crystal synthesized at temperatures below 300°C in several solutions. The characteristic FT-IR spectra of the single crystal grown in H_2SO_4 and HCl solutions are identical to those for the single crystal grown in H_3PO_4 solution. The spectra are characterized by strong absorptions between 1250 and 1100 cm^{-1} due to P-O stretching and near 500 cm^{-1} due to O-P-O bending, respectively, and those in the region 700 to 600 cm^{-1} involve some combination of P-O and Ga-O stretching [17].

3.3. Growth of GaPO_4 single crystal

Growth runs of GaPO_4 single crystals were carried out using the several growth conditions and methods. The growth features of GaPO_4 single crystals did not depend on the growth method, but varied with the kind of solvent and growth temperature.

As shown in Table I, the growth rates along the x and z axes of GaPO_4 single crystals synthesized in H_2SO_4 and HCl solutions are higher than those in

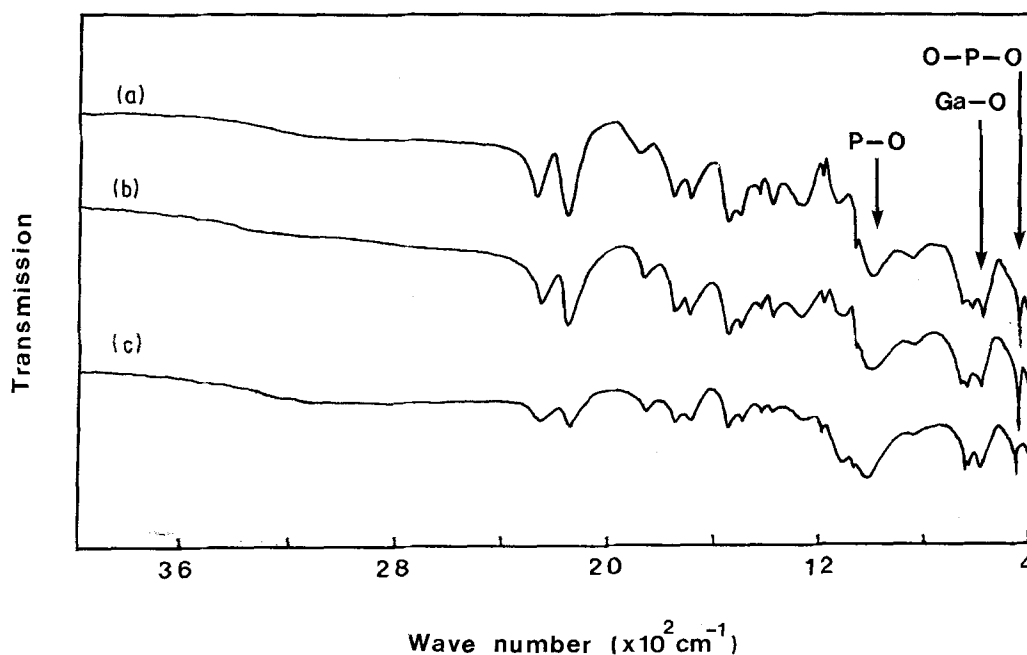


Figure 2 FT-IR spectra of GaPO_4 single crystals synthesized at temperatures below 300°C in several solutions. (a) $3\text{ M H}_2\text{SO}_4$, (b) 3 M HCl , (c) $3\text{ M H}_3\text{PO}_4$.

TABLE I Growth rates of GaPO₄ single crystals synthesized by temperature increase method at 210 to 240 °C for 3 days in several solutions.

Axis	Growth rate		
	3 M H ₃ PO ₄ (mm day ⁻¹)	3 M HCl (mm day ⁻¹)	3 M H ₂ SO ₄ (mm day ⁻¹)
V _x	0.14	0.11	0.20
V _y	0.07	0.10	0.01
V _z	0.27	0.31	0.26

H₃PO₄ solution, respectively. Such a growth behaviour is similar to that of AlPO₄ single crystals grown in HCl and H₂SO₄ solutions [10, 11]. The growth rates of seed crystals have also been examined for the hydrothermal conditions of temperature and heating rate over the range 150 to 300 °C and 2 to 10 °C day⁻¹. As a result, the hydrothermal conditions for the high growth rates of GaPO₄ single crystals were a temperature of 210 to 290 °C and a heating rate of 10 °C day⁻¹, where solubility of GaPO₄ was large enough to proceed the growth. Growths of the single crystals were achieved by slow heating of the saturated solution at the constant heating rate, i.e. the temperature increase method. Under such conditions, the single crystals of about 2 × 1 × 3 mm³ in size could be grown spontaneously in several solutions without any seed crystal. Fig. 3 shows GaPO₄ single crystal grown hydrothermally in 3 M HCl solution. On the other hand, the growth rates along the *c* axis of seed crystals in several solutions are as follows: 3 M H₃PO₄; 0.06 mm day⁻¹, 3 M HCl; 0.08 mm day⁻¹, 3 M H₂SO₄; 0.05 mm day⁻¹. From the above results, the hydrothermal conditions for the growth of large GaPO₄ single crystals are a temperature of 210 to 290 °C, a heating rate of 10 °C day⁻¹ and a solvent of 3 M HCl solution.

3.4. Morphology and density of grown single crystals

The single crystals grown at temperatures below 200 °C tended to be bounded by small major rhombohedral (10 $\bar{1}$ 1) faces. The morphologies of single crystals grown at temperatures over the range 210 to 430 °C mainly exhibited five types. Fig. 4 shows the gradual changes of morphology of grown crystals with growth conditions. The single crystals have morpho-

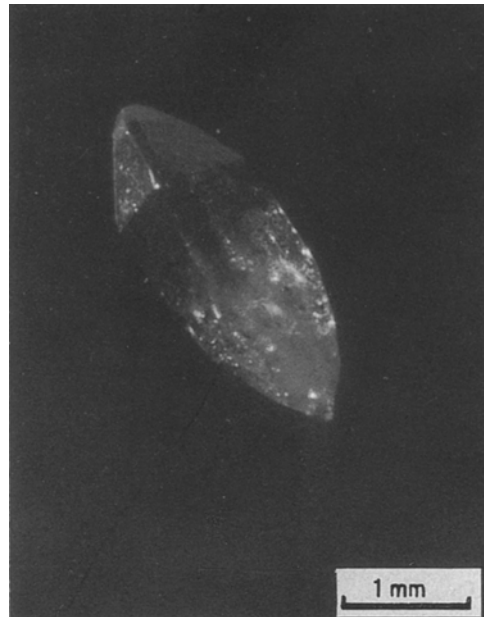


Figure 3 Microscopic photograph of GaPO₄ single crystal grown hydrothermally by the temperature increase method at 210 to 290 °C for 8 days in 3 M HCl solution.

logies bounded by prismatic (10 $\bar{1}$ 0), small major rhombohedral (10 $\bar{1}$ 1) and minor rhombohedral (01 $\bar{1}$ 1) faces at the early stage, and grew with well developed basal (0001) faces by increasing the growth temperature [6–8].

Table II shows the dislocation densities determined by etch pits on the (01 $\bar{1}$ 1) face of single crystals grown at 210 to 290 °C in several solutions. Dislocation densities of GaPO₄ single crystals grown in 3 M H₃PO₄ solution were lower than those in 3 M HCl and 3 M H₂SO₄ solutions. The present results indicate that the high quality single crystal of GaPO₄ can be obtained in 3 M H₃PO₄ solution.

TABLE II Dislocation densities on the (01 $\bar{1}$ 1) face of GaPO₄ single crystals grown hydrothermally by the temperature increase method at 210 to 290 °C for 8 days in several solutions.

Solution	Dislocation density (cm ⁻²)
3 M H ₃ PO ₄	10 ⁴ –7 × 10 ⁵
3 M HCl	10 ⁴ –8 × 10 ⁵
3 M H ₂ SO ₄	10 ⁴ –10 × 10 ⁵

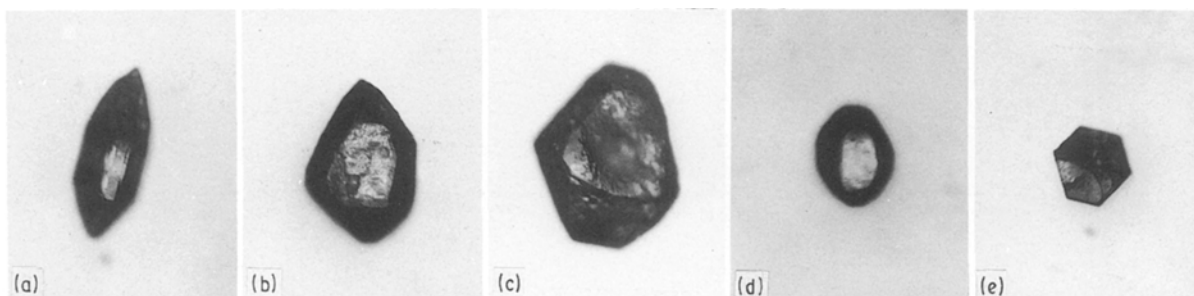


Figure 4 Morphological changes with growth temperature in several solutions: at 210 to 400 °C (a–c), 400 to 430 °C (d–e) in 3 M H₃PO₄ solution, at 210 to 370 °C (a–c), 370–430 °C (d–e) in 3 M HCl solution and at 210–270 °C (a–c), 270–430 °C (d–e) in 3 M H₂SO₄ solution.

4. Conclusion

GaPO₄ particles were synthesized as a single phase by the hydrothermal treatment of GaPO₄·5H₂O at 170 °C for 3 days in 3 M H₃PO₄ solution. H₃PO₄, HCl and H₂SO₄ solutions were found to be effective solvents for the growth of GaPO₄ single crystal. The hydrothermal conditions for the growth of large GaPO₄ single crystals are as follows: temperature, 210 to 290 °C; heating rate, 10 °C day⁻¹; solvent, 3 M HCl solution. The single crystals grown at temperatures over the range 210 to 430 °C exhibited gradual changes of morphology, i.e. the crystals have morphologies bounded by prismatic (10 $\bar{1}$ 0), small major rhombohedral (10 $\bar{1}$ 1) and minor rhombohedral (01 $\bar{1}$ 1) faces at the early stage, but the crystals were grown with well developed basal (0001) faces by increase in the growth temperature. High quality single crystals of GaPO₄ have been hydrothermally grown at 210 to 290 °C in 3 M H₃PO₄ solution.

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