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Hydrothermal Growth of $GaPO_4$ Single Crystals in HCl Solution

Pan-Chae Kim and Shin-Ichi Hirano*
Department of Inorganic Materials Engineering, Dongshin University

*Department of Applied Chemistry, Faculty of Engineering, Nagoya University

ABSTRACT

The hydrothermal growth of $GaPO_4$ single crystals was carried out by the horizontal temperature gradient method. The most promising solvents for the crystal growth of $GaPO_4$ are H_3PO_4 and HCl solutions. Single crystals have been hydrothermally grown at temperatures over the range 210-290 °C in these solutions with seed crystals. The growth rates in HCl solution were higher than that for comparable conditions in H_3PO_4 solution. Morphologies of crystals grown at temperatures below 200 °C tended to be bounded by small major rhombohedral($10\bar{1}1$) faces. In the temperature range from 200 to 430 °C, the single crystals have morphologies bounded by prism($10\bar{1}0$), 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.

1. INTRODUCTION

The crystal structure of orthophosphate crystals $M^{3+}P^{5+}O_4$(M=Al, Ga, Fe or Mn) is isomorphic to α-quartz. These single crystals have a unit cell dimension which is almost doubled along the c-axis in comparison with α-quartz, owing to the substitution of alternate Si^{4+} sites with M^{3+} and P^{5+} ions [1,2]. It was well known that the single crystals of $AlPO_4$ have been attracted by its large piezoelectric coupling constants(several times those of α-quartz) and temperature stability of frequency of certain orientations [3-8]. Because of these properties, use in SAW(Surface Acoustic Wave) and other piezoelectric devices is likely. $GaPO_4$ single crystals with a similar structure to $AlPO_4$ single crystals have been expected to exhibit the similarity of its properties.

The low-temperature(alpha) forms of $AlPO_4$ and $GaPO_4$ single crystals are stable below 584 and 976 °C, respectively, and suffer a phase transition and the decomposition [9-14]. This fact suggests that the hydrothermal growth method is appropriate for growing these single crystals. Most of the growh methods now used are based on the vertical reverse temperature gradient method employed by Stanley [15] and the horizontal temperature gradient method proposed by Krau et. al. [16], where the single crystals have been hydrothermally grown by slow heating of the saturated solution in an autoclave. The growths of these single crystals are usually difficult due to its negative temperature coefficient of solubility [14,17-

23]. In the past few years, many works have been studied on the growth of these single crystals and the feasibility of large crystals. In most studies, $GaPO_4$ single crystals have been hydrothermally grown at temperatures below 300 °C in H_3PO_4 solution [14,22-27]. However, detailed data on the crystal growth of $GaPO_4$ have not been available in HCl solution. This paper describes the hydrothermal conditions for the growth of large $GaPO_4$ single crystals and the morphology of crystals grown in HCl solution.

2. EXPERIMENTAL

The starting particles of $GaPO_4$ for the crystal growth were prepared by the solid state reaction using Ga_2O_3(99.99% purity) and $NH_4H_2PO_4$(>99.0% purity) mixture and the subsequent hydrothermal treatment in HCl solution. The apparatus and procedures for solubility measurement and growth have already been described [14,26], and were used in identical manner in this work. Typical vessels made of teflon, silica glass, platinum or gold were used for hydrothermal treatments and the growth runs of $GaPO_4$ single crystals. Growth experiments were carried out by the horizontal temperature gradient method. $GaPO_4$ particles as a nutrient were put at the low-temperature zone(i.e. dissolving region), while seed crystal was placed in the high-temperature zone(i.e. growth region), because of the negative solubility dependency of $GaPO_4$ on temperature in H_3PO_4 [14,23] and HCl solutions [28]. This arrangement is expected that the dissolved nutrient is efficiently used to grow single crystals on the seed without any occurrence of spontaneous nucleation. The analysis of prepared raw materials of $GaPO_4$ particles and grown single crystals were carried out by X-ray diffraction(XRD). The growth rates and morphologies of the grown crystals were observed by the optical microscopy.

3. RESULTS AND DISCUSSION

The solid state reaction process between Ga_2O_3 and $NH_4H_2PO_4$ has already been reported [14]. The formation reaction of $GaPO_4$ completed above 800 °C. The prepared powders treated at 1000 °C for 24h and then cooled to room temperature were composed of the low-temperature type $GaPO_4$, P_2O_5 glass and the high-temperature type Ga_2O_3. In order to prepare the $GaPO_4$ particles, these mixture powders were hydrothermally treated at 180 °C for 30h in 3m HCl solution. As shown in Fig. 1,

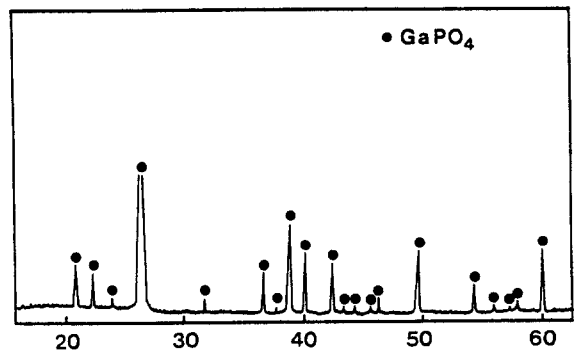


Fig. 1. X-ray diffraction profile of the low-temperature type $GaPO_4$ particles synthesized hydrothermally in 3m HCl solution at 180 °C for 30h.

the synthesized particles were confirmed to consist only of the low-temperature type of $GaPO_4$ formed as a single phase. These single phase $GaPO_4$ particles were used as a nutrient for the crystal growth.

Preliminary growth experiments 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. From these results, H_3PO_4 and HCl solutions were found to be the most promising solvents to grow $GaPO_4$ single crystals. The temperature coefficients of solubility of $GaPO_4$ in these solutions were negative over the range 150-300 °C and $GaPO_4$ was the stable phase. However, the solubility in HCl solution was greater than that for comparable conditions in H_3PO_4 solution. This result indicates the great advantage of HCl solution for obtaining large crystals.

On the basis of the preliminary experiments, further growth runs were conducted at the following conditions : temperature, 150-300 °C ; heating rate, 2.4-9.6 °C/day ; run duration, 3-8 days ; solvent, H_3PO_4 and HCl solutions. Under these conditions, 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). A schematic of the autoclave with a silica glass used for horizontal temperature gradient method is shown in Fig. 2. The nutrient is put in

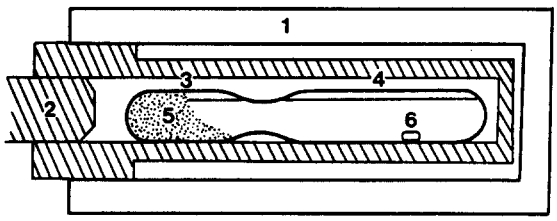
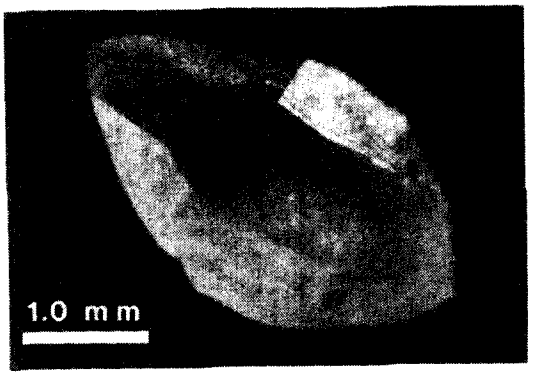
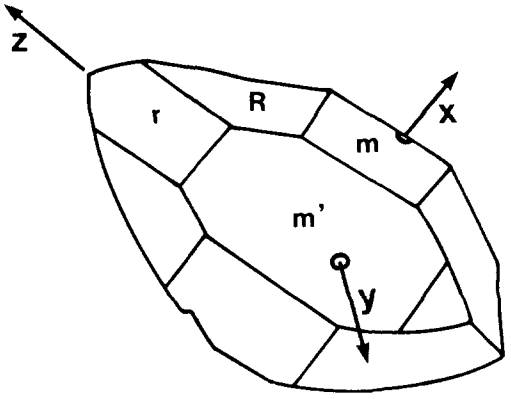


Fig. 2. Schematic of the autoclave with a silica glass used for horizontal temperature gradient method : (1) furnace, (2) Tuttle-Roy type autoclave, (3) dissolving region, (4) growth region, (5) nutrient, (6) seed.

the shortest part(low-temperature zone), while seed is placed in the largest part(high-temperature zone) ; these two regions are separated by a constriction of the silica glass vessel. A horizontal temperature gradient is established between the two zones. The growth rates along the x-and z-axis of $GaPO_4$ single crystals synthesized in HCl solution were higher than that in H_3PO_4 solution, respectively. As a result, the hydrothermal conditions for the high growth rates of $GaPO_4$ single crystals were a temperature of 210-290 °C, a heating rate of 9.6 °C/day and a solvent of 3m HCl solution, where solubility of $GaPO_4$ was large enough to proceed the growth. Under such conditions, single crystals with rough surfaces and the irregular morphology were grown by the spontaneous nucleation over the two zones at the large temperature difference of 60 °C. This result indicated that the supersaturation and the growth rate were too high. It was found that an adequate supersaturation at a horizontal temperature difference of 40 °C and a large size of platinum capsule of 10㎜ inner diameter, gave the expected growth results. $GaPO_4$ single crystal of about $2\times1\times3㎜^3$ in size could be grown spontaneously in 3m HCl solution without any seed crystal as shown in Fig. 3. On the other hand, the growth rates along the z-axis of seed crystals in these solutions are as follows : 3m H_3PO_4 ; 0.06㎜/day, 3m HCl ; 0.08㎜/day, respectively. From the above results, the hydrothermal conditions for the growth of large $GaPO_4$ single crystals with euhedral morphology are a temperature of 210-290 °C, a heating rate of 9.6 °C/day, a horizontal temperature difference of 40 °C and a solvent of 3m HCl solution.





m $(1\,0\,\bar{1}\,0)$
m' $(0\,1\,\bar{1}\,0)$
R $(1\,0\,\bar{1}\,1)$
r $(0\,1\,\bar{1}\,1)$

Fig. 3. Microscopic photograph of $GaPO_4$ single crystal grown hydrothermally by the temperature increase method at 210–290 °C for 8 days in 3m HCl solution.

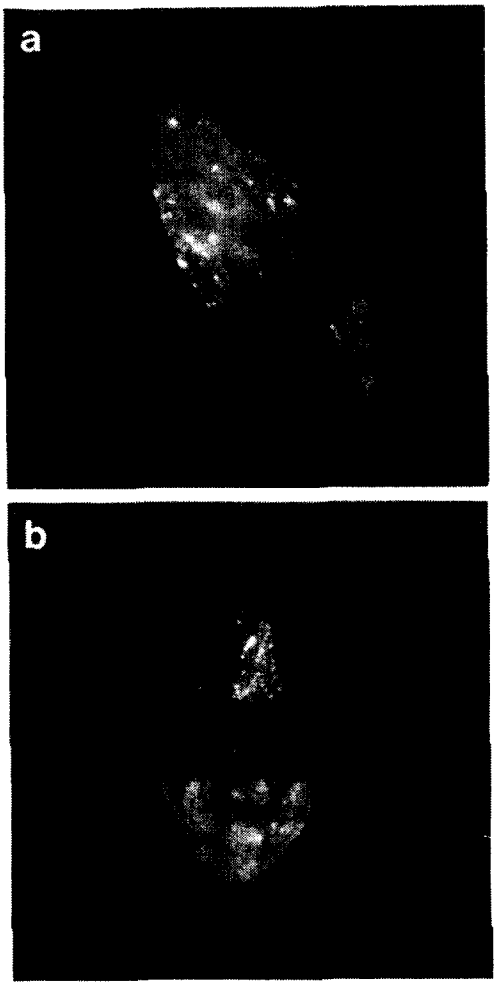


Fig. 4. Microscopic photographs of $GaPO_4$ single crystal grown hydrothermally in 3m HCl at (a) 210° and (b) 350° for 3days.

Morphologies of crystals grown at temperatures below 200 °C in 3m HCl solution tended to be bounded by small major rhombohedral$(10\bar{1}1)$ faces. In the temperature range from 200 to 370 °C, the single crystals have morphologies bounded by prism$(10\bar{1}0)$, small major rhombohedral$(10\bar{1}1)$ and minor rhombohedral$(01\bar{1}1)$ faces at the early stage (Fig. 4a), but the development of the prism$(10\bar{1}0)$ face was suppressed with the occurrence of the small major rhombohedral$(10\bar{1}1)$ and basal (0001) faces by increasing the growth temperature(Fig. 4b). At temperatures over the range 370–430 °C, the basal(0001) face is confirmed to be a more dominant face than the

other faces as shown in Fig. 5.

Fig. 5. Microscopic photograph of $GaPO_4$ single crystal grown hydrothermally in 3m HCl solution at 400 °C for 3 days.

4. CONCLUSIONS

The starting particles of $GaPO_4$ were prepared as a single phase by the solid state reaction of a stoichiometric mixture of Ga_2O_3 and $NH_4H_2PO_4$ and the subsequently by the hydrothermal treatment. HCl solution was found to be the most effective solvent to grow $GaPO_4$ single crystals. The hydrothermal conditions for the growth of large $GaPO_4$ single crystals with euhedral morphology are as follows : temperature, 210－290 °C ; heating rate, 9.6 °C/day ; horizontal temperature difference, 40 °C ; solvent, 3m HCl solution. Morphologies of crystals grown at temperatures below 200 °C in 3m HCl solution tended to be bounded by small major rhombohedral($10\bar{1}1$) faces. The single crystals grown at temperatures over the range 200－430 °C exhibited gradual changes of morphology, i.e. the crystals have morphologies bounded by prism($10\bar{1}0$), 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 increasing the growth temperature.

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