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Hydrothermal Synthesis of Gallium Orthophosphate Crystals

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Synthesis and crystal growth of $GaPO_4$ have been carried out in order to elucidate the properties of gallium orthophosphate. Single crystals were hydrothermally grown in the low temperature range from 150 to 180 °C. Solubility of $GaPO_4$ was measured under hydrothermal conditions, and the temperature coefficient of solubility was found to be negative in H_3PO_4 solution. Single crystals have morphologies bounded by the major rhombohedral $(10\bar{1}1)$ faces under lower temperature and pressure conditions. Polymorphs of $GaPO_4$ exist corresponding to low quartz type, low and high cristobalite types.

On the study of orthophosphate crystals M(III)PO_4, with M=Al, Ga, Fe, or Mn, compared with the extensive studies on berlinite ($AlPO_4$), little has been done on other crystals. It is well known that the single crystal of $AlPO_4$ has a larger piezoelectric coupling constant than quartz.[1] Single crystals of $GaPO_4$ which have a similar structure to $AlPO_4$ have potential as a promising material with interesting piezoelectric properties. However, the synthesis and properties of $GaPO_4$ single crystals have not been well investigated. This work describes the following studies; (1) synthesis of $GaPO_4$ particles as a single phase, (2) measurement of solubility of $GaPO_4$ in 4 mol dm^{-3} H_3PO_4 hydrothermal solution, (3) growth of $GaPO_4$ single crystals in H_3PO_4 solution at low temperatures below 180 °C, (4) phase transition of $GaPO_4$ single crystals.

Experimental

The starting particles of $GaPO_4$ were prepared by the solid state reaction of a stoichiometric mixture of Ga_2O_3 (99.99% purity) and $NH_4H_2PO_4$ (>99.0% purity) at 1000 °C for 24 h, and subsequently by the hydrothermal treatment at 180 °C and 14.7 MPa for 24 h in 4 mol dm^{-3} H_3PO_4 solution.[2,3] The hydrothermal runs were carried out in a test-tube type pressure vessel. The temperature was controlled with a calibrated chromel–alumel thermocouple set in the pressure vessel. The pressure was measured with a calibrated Heise gauge with an accuracy of ±0.5%. The solubility was determined by the weight loss method with a gold capsule of about 0.4 cm^3 in inner volume with recrystallized powders. The powders and H_3PO_4 solution were sealed hermetically in the gold capsule, and placed in a pressure vessel. Solubility runs were carried out at desired temperatures and pressures. Equilibrium was achieved after 3 d. Therefore, the solubility was measured by experimental runs for longer than 3 d, which were found to be enough to reach the equilibrium by preliminary experiments. The pressure vessel was quenched into cold water, the capsule was cut-open, and the powders were rinsed on a filter, dried and weighed. Synthesis runs of $GaPO_4$ single crystals were carried out by the following two methods because of its negative temperature coefficient of solubility; runs were performed by an inverse method with the nutrient in a lower temperature region and the others by the temperature increase method. The hydrothermal growth conditions are a temperature of 150—180 °C, a pressure of 14.7 MPa, a solvent of 4 mol dm^{-3} H_3PO_4 and a run duration of 3—7 d. The morphology of the grown single crystals was observed by optical microscopy. Phase transitions of $GaPO_4$ single crystals were investigated by DTA and XRD.

Results and Discussion

Synthesis of the Starting Particles. In order to investigate the solid state reaction process between Ga_2O_3 and $NH_4H_2PO_4$, DTA-TG analysis was carried out at a heating and cooling rate of 10 °C min^{-1} (Fig. 1). Endothermic peaks at about 200 and 300 °C are ascribed to the two step decomposition reactions of $NH_4H_2PO_4$.[2] The partial reaction of Ga_2O_3 with P_2O_5 produced from $NH_4H_2PO_4$ took place at about 450 °C to form $GaPO_4$, associated with amorphous $Ga(H_2PO_4)_3$ compound. The XRD indicated the formation of crystalline $GaPO_4$. Amorphous $Ga(H_2PO_4)_3$ decomposed to $Ga(PO_3)_3$ at about 550 °C. $GaPO_4$ was formed in a highly crystallized state associated with evaporation of P_2O_5 above about 850 °C. The formation of $GaPO_4$ crystalline powders took place by the decomposition of $Ga(PO_3)_3$ to loose P_2O_5, at which a little weight loss occurred. The products reacting up to 800 °C were consist with Ga_2O_3, P_2O_5, $GaPO_4$, and $Ga(PO_3)_3$. The formation reaction of $GaPO_4$ completed above 800 °C. The prepared powders treated at 1000 °C for 24 h and then cooled to room temperature were composed of the low temperature type $GaPO_4$, P_2O_5 glass and the high

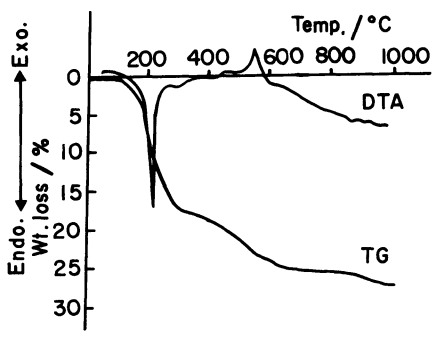

Fig. 1. Thermogravimetric and differential thermal analysis of the reaction product between Ga_2O_3 and $NH_4H_2PO_4$.

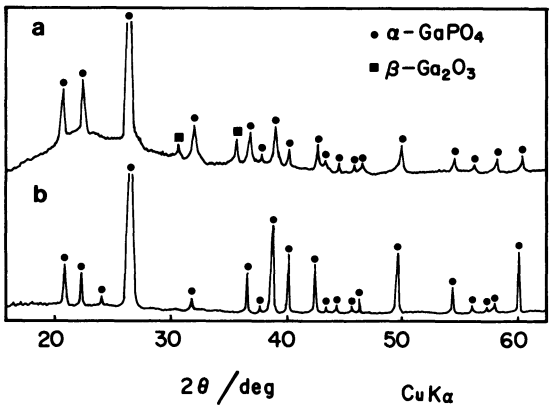

Fig. 2. X-Ray diffraction profiles of Ga_2O_3–$NH_4H_2PO_4$ mixture, (a) reacted twice at 1000 °C for 24 h, and (b) hydrothermally treated at 180 °C and 14.7 MPa for 24 h in 4 mol dm^{-3} H_3PO_4 solution.

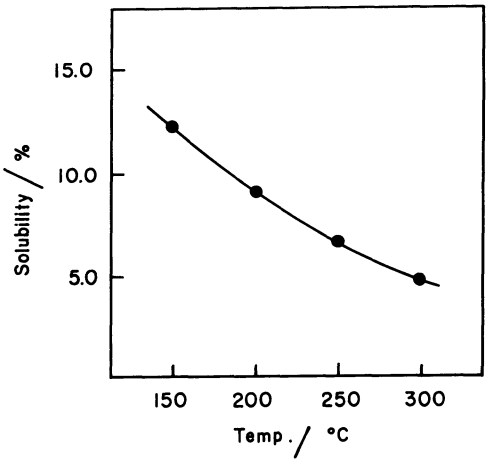

Fig. 3. Weight percent solubility of $GaPO_4$ as a function of temperature at 14.7 MPa in 4 mol dm^{-3} H_3PO_4 solution.

temperature type Ga_2O_3 as shown in Fig. 2 (a). The above results indicate a solid state reaction process to form $GaPO_4$ as follows:

$$2NH_4H_2PO_4 \rightarrow P_2O_5 + 2NH_3\uparrow + 3H_2O\uparrow \text{ (200 and 300 °C)}$$

$$Ga_2O_3 + 3P_2O_5 + 6H_2O \rightarrow 2Ga(H_2PO_4)_3 \text{ (ca. 450 °C)}$$
$$(Ga_2O_3 + P_2O_5 \rightarrow 2GaPO_4)$$

$$Ga(H_2PO_4)_3 \rightarrow Ga(PO_3)_3 + 3H_2O\uparrow \text{ (ca. 550 °C)}$$

$$Ga(PO_3)_3 \rightarrow GaPO_4 + P_2O_5\uparrow \text{ (>800 °C)}$$

In order to prepare the $GaPO_4$ particles as a single phase, these mixture powders were hydrothermally treated at 180 °C and 14.7 MPa for 24 h in 4 mol dm^{-3} H_3PO_4 solution. As shown in Fig. 2 (b), it was confirmed that only the low temperature type of $GaPO_4$ formed as a single phase. Single phase $GaPO_4$ particles were used for the solubility measurement and crystal growth.

Solubility. Solubilities in 4 mol dm^{-3} H_3PO_4 hydrothermal solution were measured as a function of temperature and pressure over the range 150—300 °C and 14.7—44.1 MPa. Figure 3 shows the solubility of $GaPO_4$ as a function of temperature at 14.7 MPa in 4 mol dm^{-3} H_3PO_4 solution. In turns out that the temperature coefficient of solubility at constant pressure, $(\partial S/\partial T)_p$, is negative over the range 150—300 °C. This fact indicated several features of importance to crystal synthesis, i.e. it is eventually required to proceed the crystal growth with supersaturation provided by a temperature difference under hydrothermal conditions where the nutrient was sustained in the low temperature region of the pressure vessel. The solubility was re-plotted as a relation of log (solubility) with $1/T$, in order to investigate the dissolution behavior of $GaPO_4$ in 4 mol dm^{-3} H_3PO_4

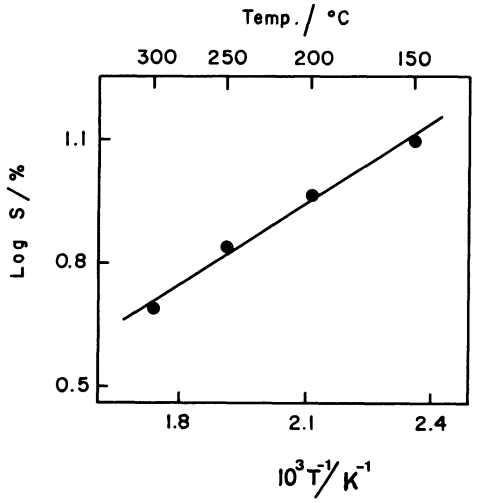

Fig. 4. Log solubility (Log S) of $GaPO_4$ as a function of $1/T$ at 14.7 MPa in 4 mol dm^{-3} H_3PO_4 solution.

$$S = \frac{\text{Wt. of dissolved } GaPO_4}{\text{Wt. of } H_3PO_4 \text{ solution}} \times 100\ (\%)$$

hydrothermal solution at 14.7 MPa (Fig. 4). The figure reveals that the van't Hoff equation was well obeyed. From the slope of Fig. 4, the heat of dissolution with the solvent, ΔH, was calculated to be about −5.4 kJ mol^{-1}. Figure 5 shows the solubility of $GaPO_4$ as a function of pressure in 4 mol dm^{-3} H_3PO_4 solution at constant temperature. The result indicates that the solubility increases with pressure under these conditions. Therefore, the general solubility behavior of $GaPO_4$ at low concentrations of H_3PO_4 solution is similar to that at relatively high concentrations.[3] However, as far as the growth experiment is concerned, the concentration of hydrothermal solvent must be especially considered because the viscosity of H_3PO_4 solution increases with increase of concentra-

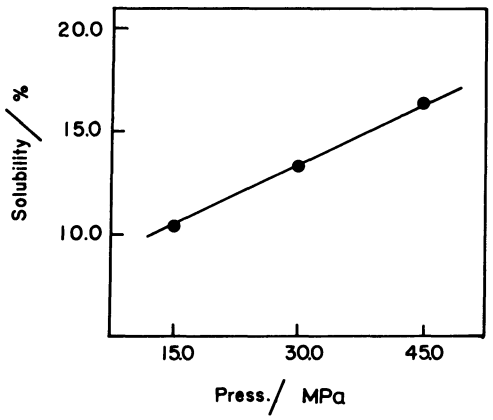

Fig. 5. Weight percent solubility of $GaPO_4$ as a function of pressure at 180 °C in 4 mol dm^{-3} H_3PO_4 solution.

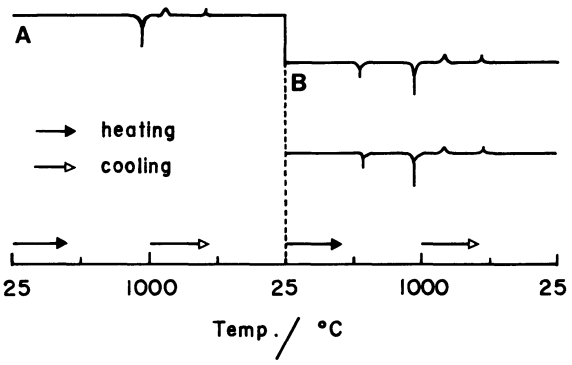

Fig. 7. Typical differential thermal analysis curves of $GaPO_4$ heated and cooled at 10 °C min^{-1}, (A) the first $GaPO_4$ run, and (B) the second $GaPO_4$ run of reverse changes.

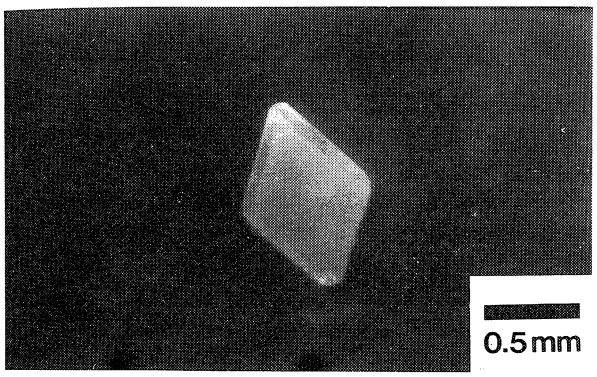

Fig. 6. Microscopic photograph of an α-quartz type $GaPO_4$ single crystal grown hydrothermally in 4 mol dm^{-3} H_3PO_4 solution at 150—180 °C and 14.7 MPa for 3 d.

tion such as 4 mol dm^{-3} H_3PO_4 solution; 4.5×10^{-3} Pa s, 6 mol dm^{-3} H_3PO_4 solution; 5.0×10^{-3} Pa s and 7.25 mol dm^{-3} H_3PO_4 solution; 5.6×10^{-3} Pa s. It becomes more difficult to avoid taking up the highly viscous solution within grown single crystals in highly concentrated solution.

Synthesis of $GaPO_4$ Single Crystals. Based on the results of solubilities, preliminary synthesis runs were carried out under the following conditions: temperature, 150—180 °C; heating rate, 10 °C d^{-1}; pressure, 14.7 MPa; run duration, 3 d; solvent, 4 mol dm^{-3} H_3PO_4 solution. Under these conditions, synthesis of single crystals was achieved by heating the saturated solution at the constant heating rate, i.e. the temperature increase method. As a result, spontaneously nucleated crystals were obtained at the lower part of the gold capsules (higher temperature region) and a typical grown crystal is shown in Fig. 6. At lower growth temperature in 4 mol dm^{-3} H_3PO_4 solution, typical grown crystals tended to be bounded by well developed major rhombohedral ($10\bar{1}1$) faces. The alternative technique was applied to grow $GaPO_4$ crystals, i.e. the inversely placed method, at 180 °C and 14.7 MPa in 4 mol dm^{-3} H_3PO_4 solution for 7 d. In a gold capsule, nutrient was set in a basket at the upper (cooler) part and the seeds were placed at the lower (hotter) part. Consequently, seeds were suspended in the hotter region and the excess nutrient in the cooler region. Also, a modified technique was used, that is the combination of the temperature increase method with inversely placed arrangement under several conditions. The growth features of the crystals did not depend on the growth method, but varied with the growth condition, e.g. at 240 °C and 25 MPa in 7.25 mol dm^{-3} H_3PO_4 solution, the crystals tended to be bounded by prism ($10\bar{1}0$) faces and terminated by small major rhombohedral ($10\bar{1}1$) faces and minor rhombohedral ($01\bar{1}1$) faces.[3]

Phase Transition of $GaPO_4$ Single Crystals. A few studies of phase transition on $GaPO_4$ have been reported.[4-6] However, the transition behavior has not been clarified yet with use of single crystals. In this work, the phase transitions of $GaPO_4$ single crystals were studied by the X-ray diffraction method and by the differential thermal analysis technique. The starting single crystals of $GaPO_4$ were identified by X-ray diffraction at room temperature. It was confirmed to consist of only the low temperature quartz type of $GaPO_4$. Typical differential thermal analysis curves for $GaPO_4$ single crystals are shown in Fig. 7. In the curve (A) of the first cycle run, the transition temperature with endothermic peak was observed at about 976 °C on the heating cycle, and those with exothermic peaks at about 915 and 576 °C on cooling. In the second heating cycle (B), the transition temperature with endothermic peaks were observed at about 608 and 957 °C on heating, and those with exothermic peaks at about 928 and 576 °C on cooling, respectively. The behavior of phases at the transition temperature was investigated by X-ray diffraction on the quenched

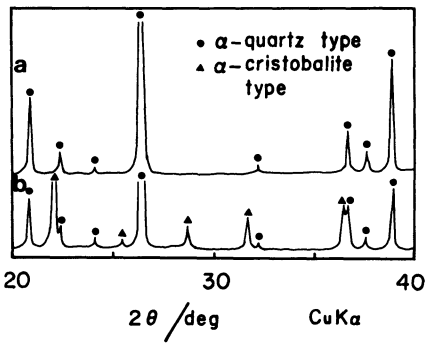

Fig. 8. X-Ray diffraction profiles of the starting $GaPO_4$, (a) the first $GaPO_4$ form, and (b) the second $GaPO_4$ form (in the data of Fig. 7).

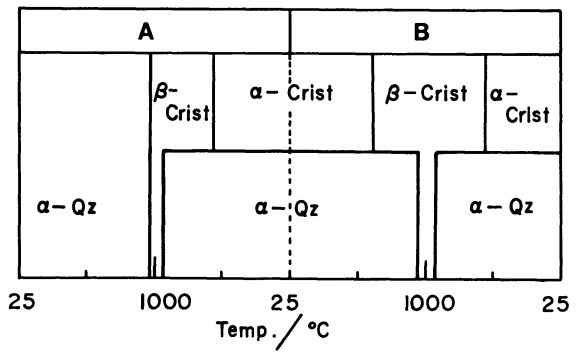

Fig. 9. The phase transition scheme of $GaPO_4$, (A) curve A, and (B) curve B of differential thermal analysis (in the data of Fig. 7).
α-Qz; low temperature quartz type, α-Crist; low temperature cristobalite type, β-Crist; high temperature cristobalite type.

specimens. In the curve (A) of the first run, it is shown that the phase transition from α-quartz type to β-cristobalite type $GaPO_4$ at around 970 °C on heating occurs, while on cooling, β-cristobalite type $GaPO_4$ was partially transformed to α-quartz type $GaPO_4$ and β-cristobalite type remained untransformed was subsequently transformed to α-cristobalite type $GaPO_4$. In the curve (B) of the second run, the phase transition from α-cristobalite type to β-cristobalite type $GaPO_4$ was observed at 608 °C. The α-quartz type transformed to β-cristobalite type $GaPO_4$ at 957 °C on heating, and the phase transition behavior on cooling was similar to the curve (A). From the above results, the starting phase of the first run was composed only of α-quartz type $GaPO_4$ of a single phase as shown in Fig. 8 (a). After cooled to room temperature from 1000 °C , α-quartz type and α-cristobalite type $GaPO_4$ coexisted, as shown in Fig. 8 (b). The results of these phase transitions were summarized in Fig. 9 on cycles.

Conclusion

α-Quartz type $GaPO_4$ particles were synthesized as a single phase by the solid state reaction of Ga_2O_3 with $NH_4H_2PO_4$ and subsequent hydrothermal treatment. Solubilities of α-quartz type $GaPO_4$ were measured under hydrothermal conditions over the range 150—300 °C and 14.7—44.1 MPa, and the temperature coefficient was found to be negative in 4 mol dm^{-3} H_3PO_4 solution. The solubility increased with increase of pressure in 4 mol dm^{-3} H_3PO_4 solution. The solubility of $GaPO_4$ obeyed the van't Hoff equation. The heat of dissolution with the solvent, ΔH, was about −5.4 kJ mol^{-1}. α-Quartz type $GaPO_4$ single crystals could be grown at lower temperature, pressure and concentration of solution, i.e. at 150—180 °C and 14.7 MPa in 4 mol dm^{-3} H_3PO_4 solution. Typical grown single crystals were bounded by well developed major rhombohedral $(10\bar{1}1)$ faces. On heating, the phase transition from α-quartz type to β-cristobalite type $GaPO_4$ occurred at about 976 °C. On cooling, β-cristobalite type transformed to α-quartz type $GaPO_4$ at about 915 °C, and subsequently transformed to α-cristobalite type $GaPO_4$ at about 576 °C. On heating in successive runs, the phase transition from the α-cristobalite type to the β-cristobalite type $GaPO_4$ occurred at about 608 °C, and the α-quartz type which remained untransformed was transformed to the β-cristobalite type $GaPO_4$ at about 957 °C. On cooling, the β-cristobalite type transformed to the α-quartz type $GaPO_4$ at about 928 °C, and subsequently transformed to the α-cristobalite type $GaPO_4$ at about 576 °C.

References

1) Z. P. Chang and G. R. Barsch, IEEE Trans. Sonics Ultrasonics, SU-23, 127 (1976).
2) S. Hirano, K. Shibata, K. Miwa, and S. Naka, *Jpn. J. Assoc. Cryst. Growth*, **12**, 100 (1985).
3) S. Hirano, K. Miwa, and S. Naka, *J. Cryst. Growth*, **79**, 215 (1986).
4) A. Perloff, *J. Am. Ceram. Soc.*, **39**, 83 (1956).
5) E. C. Shafer and R. Roy, *J. Am. Ceram. Soc.*, **39**, 330 (1956).
6) L. H. Cohen and W. JR. Klement, *Philos. Mag.*, **39**, 399 (1979)