
HYDROTHERMAL SYNTHESIS OF COPPER(II) PHOSPHATES

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Abstract Some copper(II) phosphates have been hydrothermally synthesized by using CuHPO$_4$·H$_2$O or Cu$_8$(HPO$_4$)$_2$(PO$_4$)$_4$·7H$_2$O as the starting materials and by treating hydrothermal processing under saturated vapor pressure conditions of 150-350°C.

With CuHPO$_4$·H$_2$O as the starting material, when hydrothermal processing in deionized water, octagonal crystals of Cu$_2$(PO$_4$)OH were produced in conditions of 150-300°C, and granular crystals of Cu$_3$(PO$_4$)$_2$ were produced in conditions of 350°C for 24 hours or more. In addition, when the processing solution was made into a 1.0 mol·dm$^{-3}$H$_3$PO$_4$ aqueous solution, a new product Cu$_3$(PO$_4$)$_2$·H$_2$O was produced in 200°C processing.

When the starting material of Cu$_8$(HPO$_4$)$_2$(PO$_4$)$_4$·7H$_2$O was hydrothermally processed in deionized water, the composition of the hydrothermal product was Cu$_2$(PO$_4$)OH under all processing conditions from 150-350°C. However, when 1.0 mol·dm$^{-3}$KF aqueous solution was used in the hydrothermal solution, the product became spherulite Cu$_5$(PO$_4$)$_2$(OH)$_4$ under conditions of 200°C for 10 hours or more and under conditions of 250°C for 10-24 hours.

Copper(II) phosphate shows antibacterial properties, and it is more effective against yellow Staphylococcus than against E. coli.

INTRODUCTION

It is anticipated that transition-metal phosphates can be used as inorganic pigments because there is absorption in the visible range based on the transition-metal ion. Among these compounds there are such already manufactured pigments as cobalt violet deep. The authors have already reported on transition-metal phosphates that can be used as inorganic pigments by clarifying the particulate properties of cobalt phosphate$^1,2$) and nickel phosphate$^3$) including the chemical composition and color of the products obtained by using the liquid phase reaction. Moreover, even in regard to copper(II) phosphate, we have already reported on particulate properties of copper(II) phosphate in which precipitation reactions were allowed to occur in several liquid phase systems$^4-6$). Thus, in this paper, we are trying to synthesize copper(II) phosphate with a color that can be used as a pigment by using a hydrothermal method.

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EXPERIMENT

PREPARATION OF THE STARTING MATERIAL

Experiments were treated with CuHPO$_4$·H$_2$O and Cu$_8$(HPO$_4$)$_2$(PO$_4$)$_4$·7H$_2$O, which were obtained by the liquid phase method of the Cu$_2$CO$_3$(OH)$_2$-H$_3$PO$_4$-H$_2$O system as the hydrothermal starting materials, as authors have already reported$^6$). Specifically, for the CuHPO$_4$·H$_2$O, 100g of 85% phosphoric acid was mixed with 100cm$^3$ of deionized water, 40g of Cu$_2$CO$_3$(OH)$_2$ was added to this while allowing decarboxylation-reaction, and when this was stirred for 24 hours at room temperature, a pale blue precipitate was obtained. Meanwhile, for the Cu$_8$(HPO$_4$)$_2$(PO$_4$)$_4$·7H$_2$O, 40g of 85% phosphoric acid was mixed with 600cm$^3$ of deionized water, 40g of Cu$_2$CO$_3$(OH)$_2$ were added to this, and when stirring for 24 hours at room temperature, a greenish pale blue precipitate was obtained.

HYDROTHERMAL PROCESSING METHOD

Using a stainless steel microtube type autoclave, 0.5g of copper(II) phosphate as the starting material and an amount of the hydrothermal processing solution (deionized water or aqueous solution of various inorganic salts) equivalent to a packing rate of 60% were put into the microtube, the temperature was raised to the prescribed setting between 150-350°C in an electric furnace, and this was maintained for the determined amount of time. At this time, the saturated vapor pressure was 0.5-16.9 MPa. After the retention time had lapsed, the autoclave was taken from the electric furnace and immediately cooled by putting into water at room temperature. The hydrothermal product obtained was filtered, washed, and vacuum dried at room temperature.

CHARACTERIZATION

To determine the color for the product obtained and for a heated sample of it, the reflectance in the visible range of 380-780nm was measured using a recording spectral photometer (SHIMAZU, UV-360). The product was identified by a X-ray diffractometer (RIGAKU, RAD-2C). The thermal changes of the product were evaluated using TG-DTA (MACSCIENCE, TG-DTA2020). The morphology of the product was observed by a scanning electron microscope (NIHON DENSHI, JEOL-JSM840). The chemical analysis of the product was the following; copper; an atomic absorption analysis (SHIMAZU, AA-640-12), phosphorus; a molybdenum blue colorimetric analysis. For the antibacterial tests, the antibacterial properties were evaluated by the pill method in which the ability to kill bacteria on agar is investigated by placing the sample, which has been formed into a pill (φ 20mm×1mm), onto agar in which E. coli. or Staphylococcus has been cultured. Tests were also evaluated by the MIC method which seeks the minimum concentration of the antibacterial agent which will kill E. coli. or Staphylococcus bacteria.

RESULTS AND DISCUSSION

SYNTHESIS USING CuHPO$_4$·H$_2$O AS THE STARTING MATERIAL

The crystal shape of the CuHPO$_4$·H$_2$O, which is the starting material, is a needle-like
crystal of ca. 1.3 × 18 μm, and by heating, the CuHPO₄·H₂O was changed to very pale green colored α-Cu₂P₂O₇ by dehydration of the water of crystallization and of the water of condensation at 155°C.

First, the X-ray diffraction pattern determined that two kinds of chemical compounds were produced when hydrothermally processing CuHPO₄·H₂O as starting material in deionized water (pH: 5.8). Specifically, when processing at 150°C for 24 hours, grayish yellow green Cu₂(PO₄)OH was produced. When processing for 48 hours at 350°C, dark blue-green Cu₃(PO₄)₂ was produced. In the past, Cu₃(PO₄)₂ was obtained by a method in which a hydrate substance of it was first synthesized by a liquid phase method, and then that was thermally dehydrated, but it was difficult to obtain a single-phase by that method. However, it was found that it is simple to obtain Cu₃(PO₄)₂ when using the hydrothermal method presented here. From the diagram, it is understood that Cu₂(PO₄)OH was produced under the conditions of 150-300°C for 3-48 hours and partially at 350°C, and that Cu₃(PO₄)₂ was produced under conditions limited to 350°C for 24 hours or more. The particle diameters of Cu₂(PO₄)OH varied as the hydrothermal processing conditions were changed. When processed at 150°C they were octagonal crystals with a long diameter of about 150 μm, and when the processing temperature was raised to 300°C, they became octagonal crystals with a diameter of approximately 20 μm. The particle is miniaturized because production of the nucleus becomes the rate-determining factor when the processing temperature is raised. Moreover, the color is also affected when the particle diameter varies. It was a grayish yellow-green when processed at 150°C based on the increase of light reflection that accompanies the reduction of particle diameter, but when processed at 300°C, it became a grayish light yellow-green. From the TG-DTA curve of Cu₂(PO₄)OH and the X-ray analysis of its thermal product, it was found that Cu₂(PO₄)OH changes to Cu₄(PO₄)₂O through the dehydration of 0.5mol of the water of crystallization by heating.

**Fig. 1** Chemical composition of the product obtained by hydrothermally processing.

**Fig. 2** Thermal changes of Cu₃(PO₄)₂·H₂O.
to 610°C. The spectral reflectance curve of the Cu₂(PO₄)OH and of the Cu₄(PO₄)₂O of the thermally dehydrated product were studied. The curve for the Cu₂(PO₄)OH was controlled by absorption from about 440nm and by reflection at 580nm or more, with 580nm being the maximum reflection; the curve for the Cu₄(PO₄)₂O of the thermal product had a maximum reflection at 550nm, and its color was a bright yellow-green. The coordination of the Cu²⁺ ions of the Cu₄(PO₄)₂O was a 6 coordination structure based on the report of the Laugt group. The color of the Cu₄(PO₄)₂O can be used as a new green pigment.

When changing the processing solution to 1.0 mol·dm⁻³H₃PO₄ aqueous solution, the composition of the hydrothermal product remained the same CuHPO₄·H₂O of the raw material at 150°C processing, but at 200°C processing, Cu₃(PO₄)₂·H₂O was newly produced, and when processing at an even higher temperature of 300°C or more, Cu₃(PO₄)₂ was produced even with deionized water (Fig. 1). By changing the processing solution from deionized water to H₃PO₄ aqueous solution in this way, Cu₃(PO₄)₂·H₂O was newly produced, and moreover it was found that the production range for Cu₃(PO₄)₂ widened. The particle shapes for the Cu₃(PO₄)₂·H₂O and the Cu₃(PO₄)₂ were aggregate particles of platy crystals of approximately 500μm and granular crystals of 50-100μm respectively. The thermal changes of the Cu₃(PO₄)₂·H₂O are indicated in Figure 2. The water of crystallization of the Cu₃(PO₄)₂·H₂O was dehydrated at 448°C by heating, and it changed to Cu₃(PO₄)₂ without passing through an amorphous phase. It was confirmed that great changes in the color occurred by this dehydration reaction.

SYNTHESIS WHEN Cu₈(HPO₄)₂(PO₄)₄·7H₂O WAS THE STARTING MATERIAL

Cu₈(HPO₄)₂(PO₄)₄·7H₂O is a platy crystal of ca. 1.5 × 2.2 μm, and when heating, the water of crystallization of the Cu₈(HPO₄)₂(PO₄)₄·7H₂O is dehydrated at 134°C, and when it is decomposed and the water of condensation is dehydrated at 230 and 270°C, it changes to amorphous Cu₃(PO₄)₂ and α-Cu₂P₂O₇. Finally, by crystallizing the amorphous Cu₃(PO₄)₂ at 625°C, it becomes a bluish pale green compound of α-Cu₂P₂O₇ and Cu₃(PO₄)₂.

When hydrothermally processing the Cu₈(HPO₄)₂(PO₄)₄·7H₂O in deionized water, the composition of the hydrothermal product changes to Cu₂(PO₄)OH under all processing conditions from 150-350°C. The crystal shape was the same octagonal crystal as when CuHPO₄·H₂O was the starting material, but it displayed a change in which the particle diameter increased when the thermal processing temperature was raised. When the processing solution was changed to 1.0 mol·dm⁻³KH₂PO₄ aqueous solution, the particle shape of the Cu₂(PO₄)OH became octahedral crystals, and when K₃PO₄ aqueous solution, which heightened the pH of the processing solution, was used, growth in the long axis direction was seen, and it became rod-like crystals of 80-200 μm. Meanwhile, when using 1.0 mol·dm⁻³H₃PO₄ aqueous solution, which lowered the pH of the process solution, the composition of the hydrothermal product was Cu₂(PO₄)OH from 150°C to 250°C, and Cu₃(PO₄)₂ was produced when processing at an elevated temperature of 300 °C or more. From this, it was found that Cu₈(HPO₄)₂(PO₄)₄·7H₂O produced a product range of Cu₃(PO₄)₂ that was broader than when CuHPO₄·H₂O was the starting material.
Furthermore, when 1.0 mol·dm⁻³ KF aqueous solution was used in the processing solution, 
\( \text{Cu}_5(\text{PO}_4)_2(\text{OH})_4 \) was produced under conditions of 200°C for 10 hours or more and under conditions of 250°C for 10-24 hours (Fig. 3). The particle shape of the 
\( \text{Cu}_5(\text{PO}_4)_2(\text{OH})_4 \) obtained was spherical shaped particles of approximately 20 μm under conditions of 200°C for 24 hours (Fig. 4), but when the processing time was lengthened, growth of individual crystals that were aggregating was observed. The authors have already reported on the preparation of 
\( \text{Cu}_5(\text{PO}_4)_2(\text{OH})_4 \) produced by the liquid phase method of \( \text{CuSO}_4\cdot\text{K}_2\text{HPO}_4\cdot\text{H}_2\text{O} \) system. The crystal shape of the 
\( \text{Cu}_5(\text{PO}_4)_2(\text{OH})_4 \) produced in that instance was an aggregate particles of platy crystals of ca.1 μm, and it differed from the shape in this method. The 
\( \text{Cu}_5(\text{PO}_4)_2(\text{OH})_4 \) was dehydrated at 490°C by heating, and passing through an amorphous phase, it changed to 
\( \text{Cu}_5(\text{PO}_4)_2\text{O}_2 \) by crystallizing at 640°C. The spectral reflectance curve of the 
\( \text{Cu}_5(\text{PO}_4)_2(\text{OH})_4 \) indicated a curve of a pale greenish blue which has a maximum reflection at 500nm; the curve of the amorphous phase immediately after thermal dehydration shifted to a maximum reflection of 570nm and became a dark yellow-red; and further, the curve of the 
\( \text{Cu}_5(\text{PO}_4)_2\text{O}_2 \) that was crystallized moved to a maximum reflection of 550nm and became a vivid yellow-green. The \( \text{Cu}^{2+} \) ion coordination of the 
\( \text{Cu}_5(\text{PO}_4)_2\text{O}_2 \), according to the report of the Laugt group, is a 5 and 6 coordination structure. The color of the 
\( \text{Cu}_5(\text{PO}_4)_2\text{O}_2 \) that was obtained by thermally dehydrating \( \text{Cu}_5(\text{PO}_4)_2(\text{OH})_4 \) is a color that can be used as a new yellow-green pigment.

**ANTIBACTERIAL PROPERTIES OF COPPER(II) PHOSPHATE**

The antibacterial properties in relation to E. coli. and yellow Staphylococcus were investigated as new functions of copper(II) phosphate. \( \text{Cu}_5(\text{PO}_4)_2\text{O}_2 \) and \( \text{Cu}_4(\text{PO}_4)_2\text{O} \),
which have colors that can be used as pigments, and \( \text{Cu}_2(\text{PO}_4)\text{OH} \), which has high stability in liquid phase, were used in these tests.

**Table 1 Antibacterial test by the MIC method.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>E.coli</th>
<th>yellow Staphylococcus</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}_2(\text{PO}_4)\text{OH} )</td>
<td>500ppm</td>
<td>125ppm</td>
</tr>
<tr>
<td>( \text{Cu}_4(\text{PO}_4)_2\text{O} )</td>
<td>125ppm</td>
<td>31ppm</td>
</tr>
<tr>
<td>( \text{Cu}_3(\text{PO}_4)_2\text{O}_2 )</td>
<td>125ppm</td>
<td>31ppm</td>
</tr>
</tbody>
</table>

![Fig.5 Antibacterial test by the pill method.](image)

First, the antibacterial properties of copper(II) phosphate in relation to E. coli. was investigated by the pill method, and it was found that E. coli. development prevention zone formed around the copper phosphate pills(Fig.5). It is assumed that the disinfectant action was produced by Cu\(^{2+}\) ions dissolving out from the pills. The area of development prevention zone that formed around the pills was \( C2<<C4=C5 \), and this tendency agreed with the solubility in liquid phase of each compound. In the results of testing yellow Staphylococcus in the same way, it was found that Staphylococcus development prevention zone were formed around the pills in the same manner as with the E. coli. However, the size was greater compared to that of the E. coli. This suggests that the antibacterial properties of copper(II) phosphate are more effective in relation to yellow Staphylococcus than E. coli. The test results using the MIC method are shown in Table 1. All of the samples had antibacterial properties, but when comparing E. coli. and Staphylococcus, it was found that a much greater effectiveness in relation to yellow Staphylococcus was manifested, and these results confirmed the results obtained in the pill test. In this way, because all the copper(II) phosphates have antibacterial properties, it is expected that they can be used as new antibacterial pigments.

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