A rapid synthesis of blue-pigment copper cyclotetraphosphate (Cu$_2$P$_4$O$_{12}$) rice-like grain nanoparticles at low temperature

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A blue-pigment copper cyclotetraphosphate Cu$_2$P$_4$O$_{12}$ was synthesized by a simple wet preparation method using copper oxide and phosphoric acid at 350 °C. The crystallite size obtained from X-ray line broadening is 53 ± 11 nm for the Cu$_2$P$_4$O$_{12}$. The FTIR spectrum of Cu$_2$P$_4$O$_{12}$ is assigned a base on the P$_4$O$_{12}^{4-}$ ion in the structure, which indicates the most striking feature of cyclotetraphosphate. XRD and FTIR results of the synthesized Cu$_2$P$_4$O$_{12}$ indicate the pure monoclinic phase with space group C$\text{2}_{1}$ (C2/c). SEM micrographs of the synthesized Cu$_2$P$_4$O$_{12}$ show rice-like grains, a porous structure and agglomerations, which are important for a specific application. The UV-Vis-NIR spectrum confirms the octahedral coordination of the Cu (II) ion and blue pigment.

Key words: Copper cyclotetraphosphate, FTIR, Rice-like grains, XRD, UV-Vis-near IR.

Introduction

Phosphate materials show interesting properties nowadays because of their wide applications in laser host, ceramic, dielectric, electric, magnetic, food additives, fuel cells, pigments, fertilizers, metal surface treatment, detergent, catalytic processes etc. [1-5]. Typical phosphate groups contain polyphosphate, cyclo-phosphate, and ultraphosphate. A polyphosphate has a chain structure in which the PO$_4$ unit shares two oxygen atoms. A cyclo-phosphate has a cyclic structure, while a ultraphosphate has a network structure [1, 6]. For many applications, phosphates are used mostly as powders and their usefulness depend on the powder properties such as particle size, surface area and morphology, it is believed that making nanostructure phosphates can improve the properties of activities, such as thermal and chemical stabilities, densification kinetics due to thier higher surface area than the bulk form and thin layers [7-9]. Consequently, the rapid development in nanoscience and nanotechnology has stimulated an increasing effort in studying nanostructures in recent years [8-10]. Such systems include phosphates, in particular, cyclo-phosphates [5-7]. The metal (II) cyclo-phosphates are relatively stable compounds, both thermally and chemically [1-3]. These compounds exhibit properties of color, anticorrosion ability and luminescence, which allow their application as special inorganic pigments [4-5]. Furthermore, these compounds are valuable phosphorus (P) and micronutrient (Ca, Cu, Mg, Fe, Mn, Co, Ni) fertilizers due to their slow solubility in soils [12, 14]. These fertilizers are called “slow releasing nutrients”.

One of the metal (II) cyclo-phosphates investigated is copper (II) cyclo-tetraphosphate Cu$_2$P$_4$O$_{12}$, which can be obtained from a mixture of phosphoric acid and suitable copper (II) salts [11-21]. Depending on the techniques used, this phosphate with various morphologies, compositions, and degrees of crystallinity has been obtained and shown to have different effects on the activities, mechanical properties and dissolusion behavior in an environment [19, 20]. Gunser et al. [16] obtained Cu$_2$P$_4$O$_{12}$ by evaporating a solution containing a slight excess (105% of the stoichiometric amount) of H$_3$PO$_4$ with copper dichloride dihydrate, followed by heating the mixture at 457 °C for 5 h in a platinum-gold crucible with a heating rate of 150 K h$^{-1}$. Onoda et al. [1] synthesized Cu$_2$P$_4$O$_{12}$ by machanochemical reforming of CuCO$_3$·Cu(OH)$_2$·H$_2$O and H$_3$PO$_4$ at 420 °C for 1 h with a heating rate of 10 K min$^{-1}$. In general, the previously reported synthetic methods employed a high temperature (> 400 °C) and a long time and have been
found to evolve green house effect gas (CO₂) [11-16]. We desire to overcome the disadvantages of the previously reported synthetic methods by using a more economical, low temperature (< 400 °C) and shorter duration (1 h) process, which will be the choice to produce technologically important materials.

To satisfy this, we report for the first time the synthesis of blue-pigment copper (II) cyclo-tetraphosphate Cu₃P₄O₁₂ rice-like grain nanoparticles by a wet preparation method at 350 °C using the mixing of copper oxide and phosphoric acid, which used a short time period and had no green house effect gas such as CO₂ emission. This method is simple, rapid, cost effective and a nontoxic route to synthesize Cu₃P₄O₁₂.

The prepared powder was characterized by a scanning electron microscope (SEM) X-ray powder diffraction (XRD), Fourier transform infrared (FTIR) and UV-Vis-near IR techniques.

Experiments

All the reagents used in this study were of A.R. grade. Following the procedure, 86.4 %w/w H₃PO₄ (14.00 ml), de-ionized water (2.00 ml) and CuO (8.00 g) were reacted in suspension state and then was vigorously stirred for 30 minutes at ambient temperature. The resulting mixture was transferred to a crucible, which was heated in the furnace at 350 °C for 1 h. The prepared mixture contained CuO (s), H₃PO₄ and H₂O reactants can be expressed as:

\[
2\text{CuO(s)} + 4\text{H}_3\text{PO}_4(\ell) + \text{H}_2\text{O}(\ell) \xrightarrow{350^\circ C} \text{Cu}_3\text{P}_4\text{O}_{12}(s) + 7\text{H}_2\text{O}(g)
\]

The dried sample was crushed into powder using a mortar and pestle. The copper content of the Cu₃P₄O₁₂ was determined by dissolving in 0.0126 M hydrochloric acid using an atomic absorption spectrophotometry (AAS, Perkin Elmer, Analyst100). The phosphorus content was determined by colorimetric analysis of the molybdophosphate complex. Powder X-ray diffraction (XRD) spectra were collected with a X-ray diffractometer (Philips PW3040, The Netherlands) with Cu Kα radiation (λ = 0.15406 nm). The A scan rate of 1 ° minute⁻¹ with a step size of 0.02 ° was employed to obtain the XRD spectra. The scherrer method was used to evaluate the crystallite size [21]. The room temperature FTIR spectrum was recorded in the range of 4000-370 cm⁻¹ with 8 scans on a Perkin-Elmer Spectrum GX FT-IR/FT-Raman spectrometer with a resolution of 4 cm⁻¹. Samples for FTIR measurements were made by pressing a mixture of KBr (spectroscopy grade, Merck) and a powdered sample. The diffuse reflectance spectrum (solid state UV-Vis-near IR) was obtained by using a Shimadzu UV-3100 spectrophotometer using an integrating sphere and BaSO₄ as the reference blank. SEM characterization was performed on a LEO SEM VP1450, a field emission system with an in-lens thermal field emission electron source.

Results and Discussion

Fig. 1 shows the XRD pattern of the blue-pigment copper (II) cyclo-tetraphosphate Cu₃P₄O₁₂. All detectable peaks are indexed as the Cu₃P₄O₁₂ with the structure in the standard data as PDF no. 731280. The results indicated that this crystal structure is in the monoclinic system with space group C2/c (Z = 4). Cell parameters were obtained from a least square refinement of the XRD data with the aid of a computer program. The least squares refinement of the indexed pattern gave a cell with dimensions: \(a = 12.11(0), b = 8.45(0), c = 9.82(3) \, \text{Å} \) and \(β = 118.41(0)^\circ\). The cell parameters of Cu₃P₄O₁₂ are close to those of the standard data PDF no. 731280 \((a = 12.56(0), b = 8.09(0), c = 9.57(4) \, \text{Å} \) and \(β = 118.58(0)^\circ\)) which are tabulated in Table 1. The average crystallite size of 53 ± 11 nm for the Cu₃P₄O₁₂ sample was calculated from X-ray line broadening of the reflections of (021), (-311), (220), (112), (-222) and (022), using the scherrer equation (i.e. \(D = 0.89\lambda /β\cosθ\)), where \(λ\) is the wavelength of X-ray radiation, \(D\) is a constant taken as 0.89, \(θ\) is the diffraction angle and \(β\) is the full width at half maximum (FWHM) [21].

![Fig. 1 XRD pattern of Cu₃P₄O₁₂.](image)

<table>
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<tr>
<th>Compounds Systems</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>Average particle size (nm)</th>
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<td>Cu₃P₄O₁₂ PDF no. 731280</td>
<td>11.88</td>
<td>8.59</td>
<td>10.14</td>
<td>119.21</td>
<td>-</td>
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<tr>
<td>This study</td>
<td>11.85(0)</td>
<td>8.63(8)</td>
<td>10.01(1)</td>
<td>118.86(5)</td>
<td>24.8 ± 4</td>
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<tr>
<td>DIF. This study - PDF</td>
<td>+0.06</td>
<td>+0.30</td>
<td>-0.06</td>
<td>-0.28</td>
<td>-</td>
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The Cu$_2$P$_4$O$_{12}$ structure is characterized by a three-dimensional framework with CuO$_6$ polyhedral linked with P$_4$O$_{12}$ rings by Cu-O-P. The basic structure unit is the centrosymmetric cyclotetraphosphate ring P$_4$O$_{12}^-$ and therefore vibrational modes can consider it as made up of the P$_4$O$_{12}^-$ anion. The vibrational modes of the P$_4$O$_{12}^-$ ion observed in the frequency range of 370-2000 cm$^{-1}$ are assigned according to the literature [22, 23]. The FTIR bands observed in Fig. 2 were matching very well with those reported by Ramakrishnan and Aruldhas [22]. The anion contains the PO$_2^-$ radical and the P-O-P bridge which differ in their bond strength. As the P-O bond strength in the PO$_2^-$ radical is stronger than in the P-O-P bridge, the stretching frequencies of the PO$_2^-$ radical are expected to be higher than those in the P-O-P bridge. The P-O bonds in the PO$_2^-$ radical show their asymmetric and symmetric stretching frequencies around 1334-1279 and 1133-1045 cm$^{-1}$, respectively. The asymmetric and symmetric stretching frequencies of the P-O-P bridge are observed in the regions of 1012-900 and 800-725 cm$^{-1}$, respectively. The symmetric P-O-P bridge stretching mode occurs at 725 cm$^{-1}$. This observed band is known to be the most striking feature of cyclotetraphosphate spectra, along with the presence of the $\nu_{\text{as}}$OPO$^-$ band. From X-ray diffraction data [11], it was shown that the crystal structure is monoclinic (space group C2/c) with a cyclic structure of the [P$_4$O$_{12}$]$^{4-}$ anion. This has been confirmed by the FTIR measurements. The bending modes are expected in the area 582-500 cm$^{-1}$ (PO$_2^-$ radical) and 461-398 cm$^{-1}$ (P-O-P bridge). The metal-O stretching usually appears in the bending mode region as the bending modes of the P-O-P bridge and absorption bands associated with these vibrations are usually very weak. The Cu atom is situated farther from the phosphorus atoms making the Cu-O bond weaker, the Cu-O stretching band are expected to be very weak and to occur at low frequency in the observed range. The weak FTIR band at 398 cm$^{-1}$ is probably due to metal-O stretching mode.

Fig. 3 displays the UV-VIS near IR spectrum of the prepared Cu$_2$P$_4$O$_{12}$ sample. It shows that the intensity of the band appearing in the visible region (280 nm) and due to d-d transitions of the active Cu(II) ions. The UV-Vis near IR spectrum of Cu$_2$P$_4$O$_{12}$ shows broad absorptions from 600 and 1200 nm, which can be attributed to a ligand-metal charge transfer from a framework electron to Cu(II). The bands observed in the visible and near infrared regions at 800 and 1044 nm correspond to the crystal field transitions between the fully occupied states $^2$B$_2g$(d$_{xy}$) and $^2$A$_{1g}$(d$_{xy}$) and the partially occupied level $^2$B$_{1g}$(d$_{x^2-y^2}$) of Cu (II) ion (3d$^9$) in octahedral site. The electronic spectra indicate that octahedrally coordinated Cu (II) cation is present in the blue color of Cu$_2$P$_4$O$_{12}$. The color changes observed in each sample are usually associated with changes in the electronic environment (e.g., ligand field effects) or with changes of the incorporated metal [24, 25].

Fig. 4 shows a SEM micrograph of blue-pigment copper cyclotetraphosphate (Cu$_2$P$_4$O$_{12}$) rice-like grain nanoparticles at low temperature.
Cu₂P₄O₁₂. The Cu₂P₄O₁₂ shows rice-like grains and a porous structure on the surface, which contains nanoparticle grains having a distribution of particle sizes of 100-1000 nm and pore sizes of 50-300 nm, respectively. The morphology of the studied compound is different from that reported by Onoda et al. [1, 3]. However the effects of rice-like grain nanoparticles and a porous structure on specific applications (pigments or the surface treatment) remain a point of contention. The result of the SEM experiment indicates that the grain sizes of Cu₂P₄O₁₂ are not consistent with the crystallite sizes in the XRD analysis because of agglomeration.

Conclusions

Blue-pigment copper cyclotetraphosphate Cu₂P₄O₁₂ was successfully synthesized by a wet preparation route using copper oxide and phosphoric acid at 350 °C for 1 h. The Cu₂P₄O₁₂ product is polycrystalline, having a crystallite size of 30-100 nm, determined by XRD. Its morphology appears to be rice-like grains in a porous structure and with agglomeration, as revealed by SEM. The vibrational bands of the P₄O₁₂⁻ anion from the observed FTIR spectra were confirmed to be the most striking feature of cyclotetraphosphate, which is in agreement with the XRD data, indicating a pure monoclinic phase with the space group is C₂/c, Z = 4. Optical measurement using a UV-Visible spectrometer showed the evidence for the Cu(II) ion in the skeletal structure and blue pigment. This synthesis method of the spherical-like Cu₂P₄O₁₂ nanoparticles is a more economical, low temperature (< 400 °C) and shorter duration (1 h) process, which will be the choice to produce technologically important materials, expected to be useful for specific applications such as ceramic pigments in the future.

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References