



Novel preparation of an ancient ceramic pigment $\text{BaCuSi}_4\text{O}_{10}$ and its performance investigation

Chaowu Zhang, Nan Zhang*, Xiayun Wang, Lina Zhang

School of Materials Science & Engineering, Shaanxi University of Science and Technology, Xi'an, 710021, PR China

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ABSTRACT

The $\text{BaCuSi}_4\text{O}_{10}$ (Chinese blue) was prepared by coprecipitation and hydrothermal process at 180°C for 20 h prior to sintering at 800°C with a final pigment of superior performance. The crystalline configuration and microstructure of the product were characterized by XRD, FTIR, SEM and TEM. The electronic structure and the valence situation were determined by XPS. The coloration was studied with colorimeter. The absorption and the luminescence properties were examined with an UV–VIS–NIR spectrometer and a spectrofluorimeter, respectively. The results show that the $\text{BaCuSi}_4\text{O}_{10}$ pigment prepared by this combined fabrication process possesses flower-like mesoporous microspheres morphology, better crystallization, clear coloration and rather qualified purity. The as-prepared $\text{BaCuSi}_4\text{O}_{10}$ pigment also shows well optical property with broadband absorption and better emission in the 800–1200 nm range. Compared with traditional solid state fabrication or only sole hydrothermal process, this novel process can also reduce hydrothermal temperature and time, and decrease calcination temperature.

1. Introduction

The appearance of the Chinese blue ($\text{BaCuSi}_4\text{O}_{10}$) pigment can be early traced back to the late Warring States period and its development reached heyday from the late Warring States period to the late Eastern Han Dynasty, meanwhile its utilization is mainly for decorative paintings and pottery [1].

Many of the artifacts those used $\text{BaCuSi}_4\text{O}_{10}$ as pigment are still well preserved nowadays, which indicates they have high physical and chemical stability [2]. The reason why the $\text{BaCuSi}_4\text{O}_{10}$ can still maintain the original color after thousands of years of severe circumstances lies in that it forms a layered $(\text{SiO}_4)_4$ tetrahedral structure framework with some Si–O bonds binding to the colorating copper Cu^{2+} ions. This stable silicate structure cannot be easily destroyed by physical or chemical processes [3,4].

For many years a lot of scientific investigations demonstrate that the $\text{BaCuSi}_4\text{O}_{10}$ pigment has superior infrared luminescent performance [5–8]. Therefore, it is widely used in biomedical analysis, archaeological imaging, optical sensors and other relative fields [5,9,10]. Recently, the materials with porous architecture have attracted much attention [11–16]. This sort of porous materials has high physical and chemical stability and then obtains extensive utilization in biotechnology, photocatalysis, optoelectrical devices and sensor technology [17–21]. A further investigation [22] indicated that the

$\text{BaCuSi}_4\text{O}_{10}$ can also develop hierarchical mesoporous microsphere configuration, which further enlarges its application range. In order to realize the industrialization application of this ancient pigment in the future, it is necessary to further investigate its novel preparation process and its performance.

Traditionally, the $\text{BaCuSi}_4\text{O}_{10}$ pigment was synthesized by solid state method long time ago. This preparation process usually used barium minerals (barite BaSO_4 or barium carbonate BaCO_3), quartz (SiO_2), the minerals containing copper and essential lead salt additives as raw materials and calcinated in $900\text{--}1000^\circ\text{C}$ for several hours. The lead salt additive plays catalytic role and it can also decrease decomposition temperature of barium mineral [4].

Later on, the preparation method of this pigment was changed from the traditional high temperature process to a soft chemical synthesis which seems to have more development prospect. Chen successfully prepared $\text{BaCuSi}_4\text{O}_{10}$ by only a sole hydrothermal process at 250°C for 48 h. Their final results showed that the as-prepared $\text{BaCuSi}_4\text{O}_{10}$ not only has well morphology, but also better performance of infrared luminescence compared with the traditional solid state process [22].

Although the solid state process can successfully prepare $\text{BaCuSi}_4\text{O}_{10}$ pigment, there are still some obvious shortcomings. The heavy metal ions such as Ba and Cu have a very slow diffusion rate even under the high temperature over 1000°C , which limits the development of grain size to micron level [23]. In addition, the contact area of the

* Corresponding author at: School of Materials Science & Engineering, Shaanxi University of Science and Technology, Xi'an, No. 6 Xuefu Road, Weiyang District, 710021, PR China.
E-mail address: zn18292440156@163.com (N. Zhang).

solid particles is relatively small, which means a higher temperature of the reaction matters for overcoming the high reaction barrier. Therefore, the solid reaction is usually not sufficient to obtain pure products but a lot of impurities within them and its crystalline particle size and morphology are also difficult to control. As for the sole hydrothermal method, although it is also a successful process to prepare the ancient pigment, it still required higher hydrothermal temperature and longer hydrothermal time. In this work, a co-precipitation and hydrothermal process combined with final crystallization calcination is used to prepare the ancient pigment $\text{BaCuSi}_4\text{O}_{10}$.

Notably, the co-precipitation and hydrothermal process combined with final calcination is a better solution to the above problems. Firstly, through the co-precipitation process the pigment precursor is formed. Then, the hydrothermal process with relatively lower temperature and shorter time will promote crystal nuclear formation and primary crystallization for $\text{BaCuSi}_4\text{O}_{10}$. The final calcination not only promotes the crystal growth but also removes the inevitable impurities of the former wet preparation process. The obtained results show that the synthesized $\text{BaCuSi}_4\text{O}_{10}$ pigment by this novel manufacturing method possesses superior characteristics of bright color, high purity and well flower-like mesoporous microspheres morphology.

2. Experiments

2.1. Sample preparation

The preparation progress diagram of the $\text{BaCuSi}_4\text{O}_{10}$ pigment sample is shown in Scheme 1.

The $\text{BaCuSi}_4\text{O}_{10}$ sample was synthesized by the coprecipitation and hydrothermal process prior to sintering at a certain temperature. The molar ratio of reactants was fixed on the composition of the target product $\text{BaCuSi}_4\text{O}_{10}$ ($\text{BaO}:\text{CuO}:\text{SiO}_2 = 1:1:4$). $\text{Ba}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.9952 g, 0.004 mmol), $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (2.1647 g, 0.008 mmol) and $\text{Cu}(\text{NO}_3)_2$ (1.8401 g, 0.008 mmol) as starting raw materials were mixed in distilled water (20 mL) in an order under intensive stirring, and then the mixture was adjusted to pH 12 with HNO_3 (0.2 mol/L) and sealed in an autoclave with a Teflon liner (25 mL). The autoclave was heated up to 180 °C and kept for 20 h, followed by cooling down to room temperature. The product was treated by washing with distilled water, drying and finally sintered at 800 °C for 5 h.

2.2. Examinations

The XRD pattern (Rigaku D/max 2200PC, Japan) of 40 kV and 40 mA with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154056 \text{ nm}$) was used to check the structure feature of the sample by scanning at the rate of $8^\circ/\text{min}$ in an angle range of $10^\circ \leq 2\theta \leq 70^\circ$ and 0.02° increments. The morphology and microstructure of the final pigment sample were observed by SEM (Hitachi S-4800, Japan) and TEM (FEI Tecnai G2 F20 S-TWIN, America).

The Commission Internationale de L'Eclairage (CIE) chromaticity coordinates were measured with an automatic whiteness meter (WSD-3C). In the CIE symmetrical color space, L^* is the lightness index,

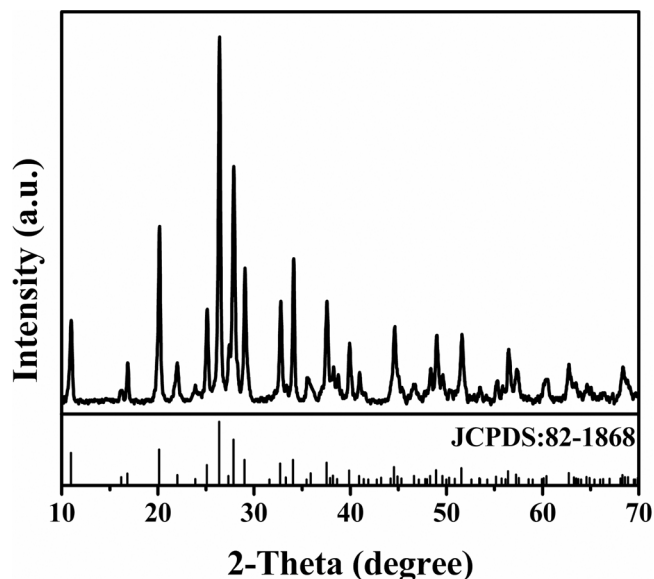


Fig. 1. XRD pattern of $\text{BaCuSi}_4\text{O}_{10}$ pigment sample.

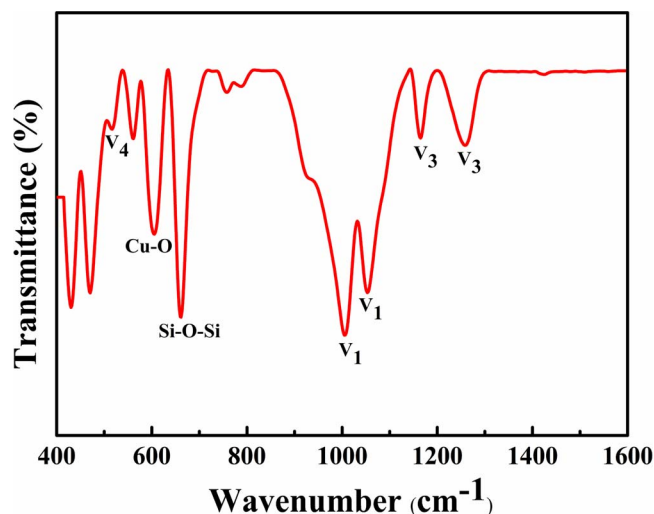
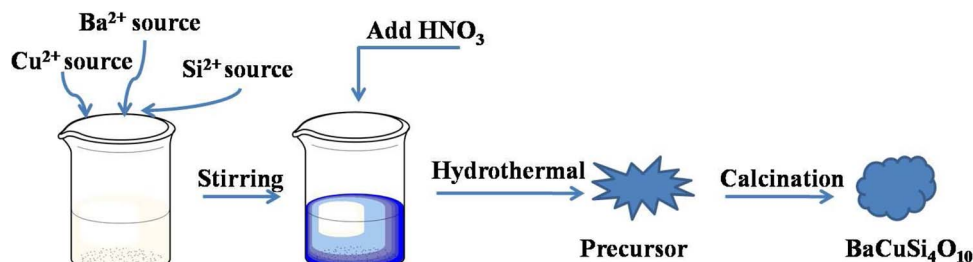


Fig. 2. FTIR spectrum of $\text{BaCuSi}_4\text{O}_{10}$ pigment.

indicating the brightness coordinates of the object in an approximately symmetrical three-dimensional color space. The brightness L^* is in the range of 0–100, in which the 0 value indicates the ideal black of absorbing all wavelength light, and the 100 value means the pure white reflecting all the light. The a^* and b^* are the chromaticity index, reflecting the chromaticity coordinates in the color space. The positive a^* value reflects the red color degree while the negative a^* value indicates the green color degree. Similarly, the positive b^* value reflects the yellow color degree while the negative b^* value indicates the blue color



Scheme 1. The preparation progress diagram of the $\text{BaCuSi}_4\text{O}_{10}$ sample.

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