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Properties of Blue Pigments SrCuSi₄O₁₀ and BaCuSi₄O₁₀

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A hydrothermal method was developed to prepare blue pigments $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$ in high yield and purity without any organic surfactants. The SEM image of $SrCuSi_4O_{10}$ indicates the presence of multi-layered microparticles with good dispersion. Hydrothermally synthetic Chinese blue $BaCuSi_4O_{10}$ are hierarchically mesoporous microspheres, which are comprised of polydisperse aggregates consisting of sheetlike nanocrystallites. The possible growth mechanism of the hierarchical structures was discussed based on TEM images. The samples show strong near-infrared luminescence ($\Phi_{EM} = 8.5$ % for $SrCuSi_4O_{10}$ and $\Phi_{EM} = 6.9$ % for $BaCuSi_4O_{10}$), which is available for optical sensors.

1 Introduction

Egyptian blue CaCuSi₄O₁₀, SrCuSi₄O₁₀ and Chinese blue BaCuSi₄O₁₀ are blue inorganic pigments with high brightness. Egyptian blue CaCuSi₄O₁₀ and Han blue BaCuSi₄O₁₀ are famous synthetic pigments, which were widely used since thousands of years ago in ancient Egypt (around 2500 BC) and in ancient China (around 1200 BC), respectively.¹ Splendor of the ancient artifacts proves their high stability even after such a long time. The source of the brilliant blue colour is the isolated square-planar Cu²⁺ chromophores in the environment of $Si_4O_{12}^{-8}$ cyclotetra-silicate layered framework.^{1,2} Near-infrared (NIR) luminescence properties of the pigments was discovered until recently, which exhibits broad absorption in the green-red part of the visible spectrum and strong emission in the range of 800-1200 nm.¹ To make the ancient pigments in keeping with the state-of-the-art requirement, research interest of the ancient blue pigments is the optimization of chemical and physical properties. The strong NIR luminescence, high chemical and photochemical stability suggest the potential applications of these pigments. Very recently Johnson-McDaniel et al. showed that CaCuSi₄O₁₀ nanosheets with primarily exposed $\{001\}$ faces derived from commercial Egyptian blue can be produced and preserve the luminescence properties.³ The grounded CaCuSi₄O₁₀ microparticles (1 - 4 µm) show good performance as ratiometric and dually lifetime referenced pH-sensoring materials in ratiometric inner filter effect sensors and optical temperature probes.⁴

Many works have focused on the synthesis with characteristics of low cost, environmentally friendliness and atom economy. Blue pigments $ACuSi_4O_{10}$ (A=Ca, Sr, Ba) were normally synthesized through solid state reaction at ca. 800–1000 °C.⁵ However, this method is hard to control the purity and morphology of the products. The operational process is also complicated and has high energy consumption. The hydrothermal method is able to carefully control the synthesis parameters (pH, temperature, pressure, etc.).⁶ The high temperature and autogenic pressure can change the solubility of reactants and facilitate specific reactions.^{7,8} It is a fundamental challenge to develop explore an alternative synthetic pathway to $ACuSi_4O_{10}$ that utilizes convenient hydrothermal conditions. It may provide an insight to the conditions under which cuprorivate forms in nature and has a good application prospect of industry.

In recent years, there has been growing interest in constructing hierarchical structures with nanoscale building block, which is used as a powerful way to integrate functional inorganic nanoparticles (NPs) into macroscale particles.^{9,10,11,12} Hierarchical structures could exhibit the advantages of the pristine building blocks and possess new physicochemical properties arising from the secondary architectures.^{13,14} Hierarchically mesoporous microspheres of silicates can serve as porous glasses, which have wide applications in industry, medicine, pharmacy research, biotechnology and sensor technology due to the high mechanical, thermal and chemical stability. Furthermore, the void space in porous particles can be used to modulate refractive index, lower density and improve the pigments' ability to withstand cyclic changes in volume.

Recently, We report the hydrothermal synthesis of Chinese purple BaCuSi₂O₆ and dark blue BaCu₂Si₂O₇.¹⁵ In this present paper, a mild hydrothermal method was developed to synthesize blue pigments SrCuSi₄O₁₀ and BaCuSi₄O₁₀ in high yield and purity. The as-prepared SrCuSi₄O₁₀ and BaCuSi₄O₁₀ are three dimensional (3D) hierarchical structures self-assembled with two dimensional (2D) sheets. The possible growth mechanism of the hierarchical structures was discussed. Large fractions of void space in the BaCuSi₄O₁₀ hierarchically mesoporous microspheres were confirmed by FIB and N₂ physisorption measurements. Furthermore, NIR luminescence properties of the hydrothermally synthetic SrCuSi₄O₁₀ and BaCuSi₄O₁₀ were quantitative studied. The pigments show strong NIR luminescence in the range of 800 - 1200 nm, which can serve as high-performance optical sensing materials.

2 Experimental Methods

2.1 Synthetic procedures

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General procedure for SrCuSi₄O₁₀ multi-layered microparticles self-assembled with nanosheets. 10 mL SrCl₂·6H₂O solution (0.5 mol/L), 40 mL Na₂SiO₃·9H₂O solution (0.5 mol/L) and 0.4 g CuO powders as starting materials were mixed together. The pH value of the solution was adjusted to 7 using HCl aqueous solution (1 mol/L), and then the concentrated ammonia solution (NH₄OH) was used to adjust the final pH value of the solution to 12. The mixture was sealed in autoclave with a Teflon liner (80 mL), then heated up to 250 °C and kept it for 48 hours, followed by cooling to room temperature by switching off the furnace. Blue powders were obtained as a single phase after washing with distilled water and drying in air. The yield of compound is 99%.

General procedure for BaCuSi₄O₁₀ hierarchically mesoporous microspheres self-assembled with nanosheets. 10 mL BaCl₂·4H₂O solution (0.5 mol/L), 40 mL Na₂SiO₃·9H₂O solution (0.5 mol/L) and 0.4 g CuO powders as starting materials were mixed together. The pH value of the solution was adjusted to 7 using HCl aqueous solution (1 mol/L), and then the concentrated ammonia solution (NH₄OH) was used to adjust the final pH value of the solution to 12. The mixture was sealed in autoclave with a Teflon liner (80 mL), then heated up to 250 °C and kept it for 48 hours, followed by cooling to room temperature by switching off the furnace. Blue powders were obtained as a single phase after washing with distilled water and drying in air. The yield of the compound is 99%.

2.2 Characterization methods

The powder products were directly used for the characterizations. The powder XRD patterns of products were collected on a PANalytical Empyrean diffractometer with Cu Ka radiation (λ =0.15418 nm) of 40 KV and 40 mA at room temperature by step scanning in an angle rang of $5^{\circ} \le 2\theta \le 90^{\circ}$ and increments of 0.0263° were employed. Lattice constants were derived from Rietveld fits using the program package FULLPROF.¹⁶ Scanning electron microscope (SEM) and EDS were performed using FIB-SEM instrument (a Helios NanoLab 600i Dual Beam System, FEI Company, with an EDS equipment (EDAX) from Ametek Company). Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) were performed on a FEI Titan electron microscope operated at 300 kV. The TEM specimens were prepared by dispersing the crushed powders in ethanol and dropping the resulting suspension onto a 200-mesh holey carbon-coated copper grid. The emission and excitation spectra of the phosphors were recorded using an Edinburgh Instruments FLS 920 spectrofluorimeter equipped with a continuous 450 W xenon lamp and using a R928 photomultiplier tube at 193 K detector coupled with a BaSO₄ coated integrating sphere. X-ray photoemission spectroscopy (XPS, Thermo ESCAlab250) experiment was performed using monochromatic Al Ka radiation (1486.6 eV). Nitrogen adsorption-desorption isotherms were collected using a TriStar 3000 (Micromeritics) nitrogen adsorption apparatus at 77 K.

3 Results and discussion

3.1 X-ray diffraction

The XRD patterns demonstrated that the hydrothermally synthetic SrCuSi₄O₁₀ and BaCuSi₄O₁₀ were single-phase. The observed powder X-ray diffraction data were refined on the basis of the tetragonal structure with space group *P4/ncc* using Rietveld-method (referenced single crystal data ICSD No. 168538 for SrCuSi₄O₁₀ and ICSD No.71864 for BaCuSi₄O₁₀). The refined parameters for SrCuSi₄O₁₀ are a = b = 7.36657(6)

Å, c = 15.5844(2) Å, V = 845.72 Å³. The refined parameters for BaCuSi₄O₁₀ are a = b = 7.440(2) Å, c = 16.097(6) Å, V = 891.03 Å³. The XRD diagrams of hydrothermally synthetic SrCuSi₄O₁₀ and BaCuSi₄O₁₀ including the raw data plots, the global fitted profile, and the difference are shown in Fig. 1. No peaks from other phases have been detected, indicating that the products are of high purity. In addition, the observed broadening diffraction peaks for hydrothermally synthetic BaCuSi₄O₁₀ indicate the nanocrystallization of the particles. However, texturize of the hierarchical structures causes preferential crystalline directions which increase their respective intensities and therefore the fitted profile stays below the measurement plots, as shown in the XRD diagrams.



Fig. 1 The XRD patterns (black curves) of the hydrothermally synthetic SrCuSi_4O_{10} and BaCuSi_4O_{10} with the Rietveld fit (red curves). The plot at the bottom is the difference between the experimental and calculated pattern intensities. The bars show the peak positions. (top) SrCuSi_4O_{10} ($R_p = 16.7$ %, $R_{wp} = 14.6$ %, $R_{exp} = 6.39$ %); (bottom) BaCuSi_4O_{10} ($R_p = 17.0$ %, $R_{wp} = 15.8$ %, $R_{exp} = 8.82$ %).

3.2 Morphology of SrCuSi₄O₁₀ multi-layered microparticles

The SEM and TEM images reveal the hierarchical structures of $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$, which also illustrates that the sample entirely consists of nearly monodispersed particles with well-defined morphology. Particles were quite uniform in size and shape. Qualitative EDXS analysis does not reveal the presence of any other elements than the compositions.

Fig. 2a shows the photograph of as-prepared $SrCuSi_4O_{10}$, which indicates the high brightness of blue powders. For preparation of $SrCuSi_4O_{10}$, the optimal pH value of the solution is 12 (the yield is 99%), and the corresponded products are multi-layered microparticles with average diameter ca. 10 µm in length. Fig. 2b shows the SEM image of monodispersed microparticles. Moreover, no other morphologies could be detected, indicating a high purity of the particles. Higher magnification SEM images shown in Fig. 2c and 2d demonstrate the detailed structural information of the multi-layered microparticles. Ultra-thin sheets packed togethter layer by layer to form the layered particles in an ordered way, which show preferential crystalline directions. The selected-area electron diffraction (SAED) pattern (Fig. 2f) of the broken single nanosheet (Fig. Journal Name

2e) exhibits square symmetry with interplanar angles of 90° within the experimental resolution limit. The pattern can be indexed exactly to the (200) and (020) reflections, which provides the [001] zone axis.



Fig. 2 (a) Photograph of as-prepared $SrCuSi_4O_{10}$ blue powders; (b, c and d) SEM images of $SrCuSi_4O_{10}$ milti-layered microparticles with the length of ca. 10 µm; (e) The TEM image of a broken nanosheet; (f) The corresponding SAED pattern provides a zone axis of [001].

3.3 Morphology of $BaCuSi_4O_{10}$ hierarchically mesoporous microspheres

Fig. 3a shows the photograph of as-prepared BaCuSi₄O₁₀, which also indicates the high brightness of blue powders. Fig. 3b and 3c show the SEM images of the BaCuSi₄O₁₀ hierarchical microspheres with good dispersion and uniform size of 8 µm, which provides a further insight into the texture of the hierarchical structure. It indicates that the thin nanosheets randomly assembled to form the microspheres without a specific orientation. SEM image (given in supporting information) of the fall-off nanosheets shows that the size is less than 1000 nm. The nanosheets are randomly attached to form the microspheres without a specific orientation, it would result lots of boundaries and void space in the structure. The Helios NanoLab 600i Dual Beam System was used to cut the hierarchically mesoporous microsphere to explore the inside structure. SEM image of the cut-face confirms that there are lots of holes in the hierarchical microsphere (shown in supporting information). These features indicated that the BaCuSi₄O₁₀ microsphere is porous hierarchical structure.

HRTEM image of a single-crystalline nanosheet was shown in Fig. 3d. The spacing of the lattice fringes equals 5.3 Å which corresponds to a lattice constant $a = b \approx 7.5$ Å assigned to the (001) plane, in agreement with XRD data of BaCuSi₄O₁₀.



Fig. 3 (a) Photograph of as-prepared BaCuSi₄O₁₀ blue powders; (b) SEM image of BaCuSi₄O₁₀ microspheres with size of 8 μ m; (c) SEM image of a BaCuSi₄O₁₀ microsphere; (d) HRTEM image of a single crystalline nanosheet.

3.4 Growth mechanism

For the preparation of BaCuSi₄O₁₀, BaCl₂·4H₂O (SrCl₂·6H₂O for SrCuSi₄O₁₀), Na₂SiO₃·9H₂O, and CuO powders were used as starting materials. The efficiency of a chemical reaction is preferred to satisfy the requirement of atom economy. The molar ratio of reactants was fixed on the composition of the target compounds (SrO : CuO : 4SiO₂ for SrCuSi₄O₁₀ and BaO : CuO : 4SiO₂ for BaCuSi₄O₁₀). The fine powder CuO was found to be an effective precursor for the hydrothermal synthesis of ACuSi₄O₁₀ (A= Sr, Ba).

The effect of reaction temperature on the formation of the products has been investigated under 220 °C, 230 °C, 240 °C, and 250 °C. The results showed that a reaction temperature higher than 230 °C was prerequisite for all the samples. The reaction time longer than 12 hours was necessary, although the target products with impurities (unreacted reactants) can be detected when the reaction time was 6 hours. The hydrothermal synthesis of these two pigments is quite sensitive to the pH value of the initial solution with the proper mineralizer. The higher or lower pH values will strongly decrease the yield of the products. The yields of both compounds with NH₄OH as mineralizer are above 99% at the optimal condition (250 $^{\circ}$ C, 48 hours and pH = 12). If using NaOH or KOH as a mineralizer, neither SrCuSi₄O₁₀ nor BaCuSi₄O₁₀ phase was detected in the obtained powders after hydrothermal treatment at 250 °C for 48 hours. The formation of the crystalline nuclei was one-step or twostep nucleation process, where solvation plays a key role.¹⁷ The pH value and NH4OH are key parameters that affects the charge property and coordination of anions according to the crystallization mechanism suggested by Barrer and co-workers.^{6,18} It seems like that the presence of NH₄OH in the solution favours the existence of the suitable building units for the $(SiO)_4$ silicate squares framework of $ACuSi_4O_{10}$. When the pH value of the solution is below 11, neither $SrCuSi_4O_{10}$ nor $BaCuSi_4O_{10}$ were detected in the final mixture powders. It needs to mention that the Chinese purple $BaCuSi_2O_6$ was detected with $BaCuSi_4O_{10}$ when pH value is ca. 11.5. It implies that the NH₄OH can also be used for the synthesis of Chinese purple $BaCuSi_2O_6$ in hydrothermal condition.¹⁵ When the pH value increased above 12, CuO phase as impurity was detected in both products.

The hierarchical structure of BaCuSi₄O₁₀ is porous microsphere self-assembled from nanosheets in a random way. Although the synthesis procedure was identical to that used for BaCuSi₄O₁₀, the morphology of SrCuSi₄O₁₀ particles was multi-layered microparticle, potentially indicating a slightly different ion state in the solution during the hydrothermal process. Hierarchical structure of SrCuSi₄O₁₀ was sensitive to the pH value of the solution and varies from multi-layered microparticles (pH=12, yield 99%) to microspheres with microplates on the surface (pH=13, yield 50%), shown in the supporting information.

On the basis of the SEM and TEM characterizations, along with the layered crystal structure of ACuSi₄O₁₀ (A=Sr and Ba), it can be concluded that the proposed fabrication of the hierarchical structures is a self-assembled process. The nanosheets as building blocks grow at the initial reaction stage, and then the sheets are prone to aggregate to lower their high surface energy. The crystalline nuclei occurred first and the further crystal growth of the primary nanosheets was strongly depended on the intrinsic crystal structure of $ACuSi_4O_{10}$. $ACuSi_4O_{10}$ have layered structures with $(SiO)_4$ silicate squares forming the structural framework, where opposite four (SiO)₄ four-ring units form new (SiO)₈ four-ring units. The square-planar Cu^{2+} chromophores in the environment of $Si_4O_{12}^{8-}$ cyclotetra-silicate layered framework and the alkaline earth cations act as relatively independent ions, located between the layered frameworks along the (001) plane as shown in Fig s1 (Supporting information). The {001} faces of the nanosheets have the lowest energy which has a lower chemical potential in comparison with other crystal faces.¹ It is therefore expected that these nanosheets have these {001} faces primarily exposed.

For SrCuSi₄O₁₀ hierachical structures, tiny nanosheets of ACuSi₄O₁₀ should be formed at first stage, then these nanosheets aggregated into 2D microplates layer by layer according to the Gibbs-Thomson law.¹⁹ For BaCuSi₄O₁₀ hierarchically mesoporous microspheres, the nanosheets directly undergo entropy-driven random aggregation to form the hierarchical structure.



Fig. 4 (a) N_2 adsorption-desorption isotherms of $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$; (b) The inset picture is pore size distribution curve of $BaCuSi_4O_{10}$ porous microspheres calculated using nonlocal density functional theory (NLDFT).

3.5 N₂ physisorption measurements

The existence of mesopores in the BaCuSi₄O₁₀ microspheres was directly corroborated by N₂ physisorption measurements. Fig. 4a shows the N₂ adsorption-desorption isotherms and the corresponding pore size distribution curves of the BaCuSi₄O₁₀ hierarchically mesoporous microspheres and the SrCuSi₄O₁₀ multi-layer particles. Compared with SrCuSi₄O₁₀, BaCuSi₄O₁₀ shows gradually increasing uptake at low relative pressures and sharp uptake at higher relative pressures with a small hysteresis. The shape of the isotherm is type IV with one H3 hysteresis at a relative pressure range of 0.8-1.0, indicating the presence of mesopores.²⁰ The H3 shape of the hysteresis loop suggests narrow slit-like mesopores, which are generally formed by sheetlike particles. It agrees well with the sheetlike morphology of the building blocks of the BaCuSi₄O₁₀ hierarchically mesoporous microspheres.²¹ The specific surface area of $BaCuSi_4O_{10}$ measured with the Brunauer–Emmett–Teller technique is 49 m² g⁻¹, and the average pore size is 15 nm obtained by a pore size distribution curve, as shown in fig. 4b. However, the specific surface area of SrCuSi₄O₁₀ measured with the Brunauer-Emmett-Teller technique is only 5.6 m² g⁻¹ without pore contribution.



Fig. 5 (a): Absorbance (dotted line), excitation (dashed line, $\lambda_{em} = 956$ nm) and emission (solid line, $\lambda_{ex} = 620$ nm) spectra of hydrothermal synthetic SrCuSi₄O₁₀ multi-layered microparticles. Inset: luminescence decay (15.8 µs, $\lambda_{ex} = 620$ nm); (b): Absorbance (dotted line), excitation (dashed line, $\lambda_{em} = 977$ nm) and emission (solid line, $\lambda_{ex} = 620$ nm) spectra of hydrothermal synthetic BaCuSi₄O₁₀ microspheres. Inset: luminescence decay (33.3 µs, $\lambda_{ex} = 620$ nm).

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3.6 Photoluminescence

Egyptian blue CaCuSi₄O₁₀, SrCuSi₄O₁₀ and Chinese blue BaCuSi₄O₁₀ exhibit excellent NIR-emission, which are attributed to the square-planar Cu²⁺ chromophores.² When irradiated by a visible laser beam (optimal excitation wavelength $\lambda_{ex} = 620$ nm), SrCuSi₄O₁₀ and BaCuSi₄O₁₀ can effectively transform this light into fluorescent near-infrared (NIR) light in the 800 – 1200 nm range. Fig. 5a shows the absorption spectrum, excitation ($\lambda_{em} = 956$ nm) spectrum, the emission ($\lambda_{ex} = 620$ nm) spectrum and the luminescence decay profile of the SrCuSi₄O₁₀ multi-layered microparticles. The center of the broad emission spectrum is at 956 nm and the luminescence decay is 15.8 µs. The broad absorption/excitation band in green-red part of the spectrum is attributable to the ${}^{2}B_{1g}$ $\rightarrow {}^{2}E_{g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ electronic transitions for the square-planar Cu²⁺ ion. Excitation due to ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ transition was not in the visible region and should occur in the NIR part of the spectrum.² Fig. 5b shows the absorption spectrum, excitation $(\lambda_{em} = 977 \text{ nm})$ spectrum, the emission $(\lambda_{ex} = 620 \text{ nm})$ spectrum and the luminescence decay profile of the BaCuSi₄O₁₀ hierarchically mesoporous microspheres. Emission spectrum of as-prepared BaCuSi₄O₁₀ shows slight red shift in comparison with that of as-prepared SrCuSi₄O₁₀. The center of the broad emission spectrum is at 977 nm and the luminescence decay is 33.3 μ s. Since the Cu²⁺ ion may be considered the only chromophore in the spectral range under investigation, the differences between the luminescence spectra of the two pigments are ascribed to a ligand-field change. This can be related to the larger size of the Ba^{2+} ion with respect to Sr^{2+} ion. Both the compounds show high luminescence quantum yields for an infrared phosphor, $\Phi_{\rm EM} = 8.5$ % for SrCuSi₄O₁₀ and $\Phi_{\rm EM}$ = 6.9 % for BaCuSi₄O₁₀. In addition, the reported λ_{max} of the emission spectrum is 914 nm for SrCuSi₄O₁₀ and 948 nm for BaCuSi₄O₁₀.⁴ The redshift of λ_{max} of the hydrothermally synthetic samples was attributed to the slightly different microstructure caused by different synthetic strategies.

4 Conclusions

We developed a facile hydrothermal synthesis of SrCuSi₄O₁₀ and BaCuSi₄O₁₀ hierarchical structures. This soft-chemistry method was optimized for easy handle, green chemistry, and high quality of products. SrCuSi₄O₁₀ hierarchically multi-layered microparticles and BaCuSi₄O₁₀ hierarchically mesoporous microspheres can be prepared in quite high yield. The preparations are sensitive to the pH value of the solution through hydrothermal treatment using NH4OH as mineralizer. Furthermore, hydrothermal synthetic BaCuSi₄O₁₀ is mesoporous microsphere self-assembled by nanosheets, which is confirmed by N₂ adsorption-desorption isotherms. Such hierarchically porous structure has wide application as porous glasses. Both samples show excellent NIR emission when excited by a visible light. The good dispersion and uniform micro-size of the particles make the products good materials for pigments and optical sensors. Future work will focus on examining the viability of the materials for use in optical sensors, pigments and porousmicrosphere-based devices.

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Notes and references

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In this work, a green chemistry strategy was developed to synthesize blue pigments $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$. And this soft chemistry method was characterized with good yield and high purity of the products. Hydrothermal synthetic $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$ exhibit hierarchical structures. Our study shows that hydrothermal synthetic $BaCuSi_2O_6$ exhibit interesting broad near-infrared luminesce.