

Ancient Egyptian Blue ($\text{CaCuSi}_4\text{O}_{10}$) Pigment by Modern Solution Combustion Synthesis Method

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Abstract

The Egyptian blue pigment, $\text{CaCuSi}_4\text{O}_{10}$, has been used in ancient Egypt from 3000 BC. This pigment consists of $\text{CaCuSi}_4\text{O}_{10}$ with variable amounts of wollastonite (CaSiO_3), high amount of Cu oxides, cuprite (Cu_2O) or tenorite (CuO). It was prepared by melting the high percentage of copper in association with lime and desert sand in the Ancient time. In this work Egyptian blue was produced by solution combustion synthesis (SCS) in homogeneous aqueous solution of composition: copper and calcium nitrates, sodium silicate and urea. This method permits chemically stable Egyptian blue fast and economic production. The Egyptian blue composition and structure obtained after SCS and calcination were studied by XRD, FTIR and SEM/EDX analysis. Crystallite size and crystal lattice parameters were calculated. An increase in combustion temperature during SHS and calcinations temperature influence Egyptian blue yield and crystallite size, slightly influence parameters of crystal lattice.

1. Introduction

The painting appears in all civilizations in human history and is an important tool of religious, ceremonial and aesthetic perceptions. From the pre-historic rock paintings of ancient cultures to modern art, paintings reflected the deep desire of artistic expression. The symbolic imagination of gods and the magical powers was a controlling factor in the choice of colors in antiquity.

One of the oldest synthetic pigments in ancient Egyptian history is Egyptian blue, $\text{CaCuSi}_4\text{O}_{10}$. The Egyptian blue is recorded as a blue pigment used in wall paintings in tombs and temples of ancient Egypt after the 4th Dynasty of the Old Kingdom (2600-2480 BC). This pigment found wide application in ancient Egyptian paintings in the Old, Middle and New Kingdoms in the Ptolemaic and Roman times. In the beginning of the 18th Dynasty (1552-1306 BC), Egyptian monuments bear witness to an explosion in the use of this pigment in tombs and temples [1, 2]. The term for this pigment, in the Egyptian language is artificial lapis lazuli. The recipe remained secret for many

centuries. It was a very expensive pigment and used sparingly [3]. Recently, Egyptian blue has been detected on Attica Lekythoi of Classical period, on wall paintings such as Macedonian tombs at Vergina and statues on the Acropolis. The composition of this pigment as otherwise called «caeruleum», described by Vitruvius in De Architectura in the 1st century BC. It was made by heating a mixture consisting of silica sand, lime (or calcareous sand), compounds of copper (or copper mineral fragments) and a fluxing (soda or plant ash) [4]. Vitruvius does not mention the component of calcium carbonate in the Egyptian blue, perhaps because the sand used in Pozzuoli, had the correct proportion of calcium to the recommendation. Because of the large amount of CaO required is considered more likely to use quartz sand, since the display amount of the calcium oxide may be entirely derived from the ashes of plants [5].

Rapid reduction of the use of Egyptian blue in Medieval and Renaissance period the was because of the fall of the Roman Empire and the consequent loss of knowledge and technology [6, 7]. This is likely to be one of the causes of the scientists and

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archaeologists have carried out experiments to analyze the composition of Egyptian blue and the techniques used to manufacture it. It is regarded as a multiphase material, cuprorivaite or Egyptian blue, that was produced by heating for several hours the combination of quartz sand, copper compound, calcium carbonate, and a small amount of some alkali (plant ash) [10]. There is a general data agreement on the melting temperature, which must be maintained between 850 and 950 °C. Above 1100 °C, in fact the Egyptian Blue decomposes [8, 9].

The shade of Egyptian blue was related to the coarseness and fineness of Egyptian blue as it was determined by the degree of aggregation of the Egyptian blue crystals. Coarse Egyptian blue, dark blue color, was relatively thick in form due to the large clusters of crystals which adhere to the unreacted quartz. Otherwise, fine-textured Egyptian blue consists of smaller clusters that are uniformly interspersed between the unreacted quartz grains and tends to be light blue in color [10]. In addition, diluted light blue, evident during the 18th dynasty and later, is used to describe the color of fine-textured Egyptian blue that has a large amount of glass formed in its composition and gives it a diluted appearance [11, 12]. This result depends on the amount of alkali added to the mixture, so with increase of alkali, more glass formed, and the appearance is more diluted [10]. If too much lime was added, wollastonite (CaSiO_3) forms and gives the pigment a green color and too much of the copper ingredients results in excesses of copper oxides like cuprite and tenorite [12].

The Egyptian blue as nanostructured composite pigment presents unique properties.

Egyptian blue's powerful and long-lived luminescence under infrared light has enabled its presence to be detected on objects which appear unpainted to the human eye [13]. This property has also been used to identify traces of the pigment on paintings produced as late as the 16th century [14]. These unique properties in conjunction with the capacity of Egyptian blue to delaminate by splitting into nanosheets after immersion in water, make Egyptian blue a unique pigment and this is a material suitable for many applications in modern science and technologies, such as in biomedicine, telecommunications, laser technology, and security inks [15, 16].

In this work Egyptian blue was produced by Solution Combustion Synthesis (SCS) – variation of self-propagating high temperature synthesis (SHS) method. SCS is efficient, low cost method for producing a plurality of commercially useful

materials [17]. SCS method became a popular approach for the preparation of nanomaterials and applied in many countries [17]. It is well known that techniques based on combustion, referred to in the literature as combustion synthesis (CS) or SHS, are effective energy saving method for the synthesis of a variety of advanced materials. In the conventional CS process, the initial reaction medium is a mixture of powder with a characteristic heterogeneous scale ranging from 1 nanometer up to several microns. This feature in combination with the high reaction temperatures up to 3000 °C makes the synthesis of nano-size materials with a surface area greater than 10 m²/g very difficult, but it is fast, economical method of producing materials in one step. A combination of CS and the reaction solution approach leads to SCS method.

The SCS is based on exothermic reaction started with self-ignition of mixture during heating, reaction is fast (typically from 0.1 to 10 cm/s), combustion temperature usually reach 700–1500 °C, combustion wave is promoted through the heterogeneous mixture by self-sustaining way resulting in the formation of the solid material without further supply energy. After an initial solution with the desired reactants is preheated at temperature (150–600 °C), it self-ignited along the entire volume (VCS) leading to the formation of fine solid products with adapted composition [17, 18]. Typically, the SCS comprises a self sustaining reaction in solutions of metal nitrates (or other oxygen containing salts) and fuels, which can be different chemical structure and composition. The reaction between a fuel and oxygen containing substances formed during the decomposition of the nitrates provides fast, high temperature interaction. The SCS method is a flexible, simple and quick process that enables the efficient synthesis of a variety of nanostructured materials, because the mixing of precursors on the molecular level and liberation of large quantities of gases, such as carbon dioxide, water, and nitrogen, result in formation of nanoscaled solid products. The composition, parameters of crystal lattice and size of the particles produced using SCS technique depend on many factors, one of them preheating temperature. All those factors influence color of pigment. In this paper, it is aimed to synthesize Egyptian blue pigment nanoparticles by application of SCS.

2. Experimental

The chemicals used in the present investigation were of analytical reagent grade and obtained from Merck (calcium nitrate), from AppliChem (urea)

and from Riedel-de Haen (sodium silicate and copper nitrate). In this study the self-propagating reaction is performed in a homogeneous aqueous solution of 25% $\text{Cu}(\text{NO}_3)_2$ + 24.6% $\text{Ca}(\text{NO}_3)_2$ + 50.4% Na_2SiO_3 + 40% Urea + 3.6% H_2O . SCS synthesis takes a few minutes, but additional heat treatment is used since reactions were not complete during this time and it was necessary additional sintering for 2 h, the sintering temperatures were 700 °C, 750 °C, 800 °C and 850 °C for 2 h with further cooling in furnace up to room temperature. The pigments were studied by X-Ray Diffraction (XRD) analysis. X-ray diffractograms were recorded using the Cu radiation of a Siemens D500 diffractometer. Scanning Electron Microscopy (SEM) (model Quanta Inspect), Energy-dispersive X-ray spectroscopy (EDS) for structure analysis and chemical analysis. The crystal lattice parameters were calculated by Bragg's law $d = (n\lambda)/(2\sin\theta)$ [19]. The mean crystallite size was calculated from Scherrer formula $D = (0.89\lambda)/(\beta\cos\theta)$ [20] based on the full width at half maximum intensity (FWHM) of the major peaks. The Infrared (IR) spectroscopic analysis was conducted and recorded using a JASCO spectrometer (model ATR PRO410 type S) in the ranges (400–1750) cm^{-1} peaks. Color characteristics – HTLM color codes (SGB, HSV) were determined by H TML color picker [21], color names determined according to classification [22].

3. Results and Discussion

SCS of mixture on the base of initial batch: 25% $\text{Cu}(\text{NO}_3)_2$ + 24.6% $\text{Ca}(\text{NO}_3)_2$ + 50.4% Na_2SiO_3 + 3.6% H_2O + 40% Urea was performed in quartz. Figure 1 demonstrate combustion process and final product – pigment Egyptian blue.

XRD analysis of SCS products of 25% $\text{Cu}(\text{NO}_3)_2$ + 24.6% $\text{Ca}(\text{NO}_3)_2$ + 50.4% Na_2SiO_3 + 3.6% H_2O + 40% Urea mixture preheated at temperatures at 700 °C, 750 °C, 800 °C and 850 °C for 2 h are presented on Fig. 2.



Fig. 1. SCS of mixture on the base of initial batch: 25% $\text{Cu}(\text{NO}_3)_2$ + 24.6% $\text{Ca}(\text{NO}_3)_2$ + 50.4% Na_2SiO_3 + 3.6% H_2O + 40% Urea: initial batch, combustion process and final product.

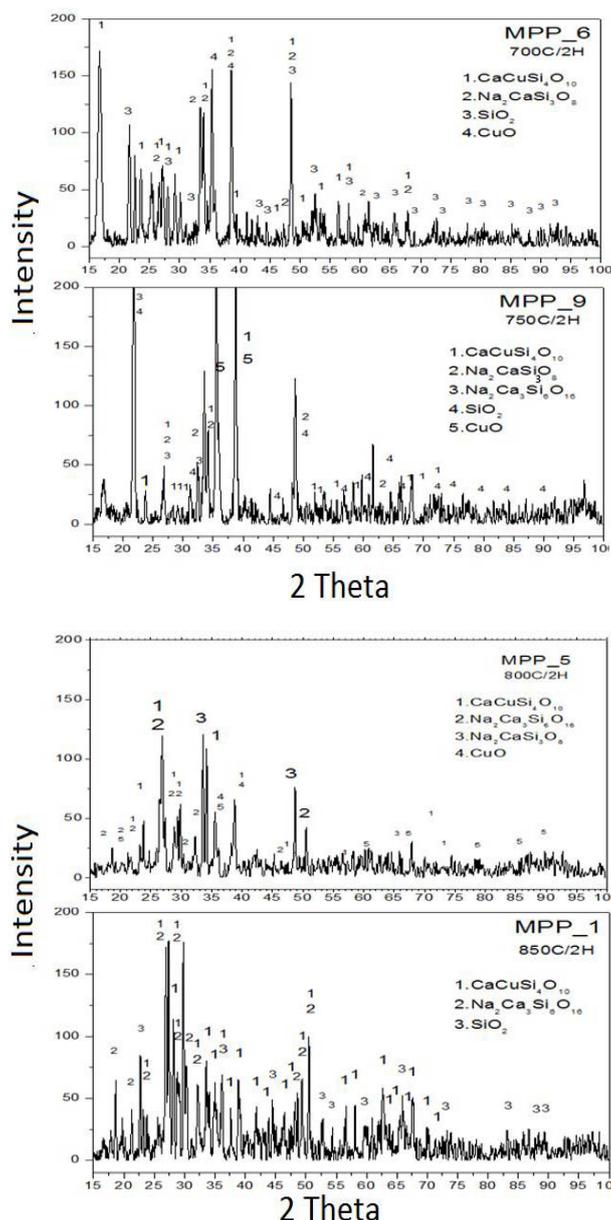
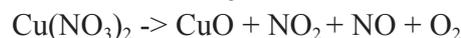


Fig. 2. X-ray powder diffractograms for Egyptian Blue, produced by SCS method at temperatures 700–850 °C.

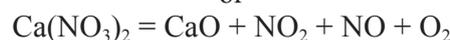
According to XRD analysis at all synthesis temperatures Egyptian blue, $\text{CaCuSi}_4\text{O}_{10}$ is present (Fig. 2). Except this phase also present wollastonite based compounds: $\text{Na}_2\text{CaSi}_3\text{O}_8$ and $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$ phases. In addition, it is observed SiO_2 and CuO especially at lower temperatures. During exothermic reaction between urea and other components of initial batch are possible following reactions:



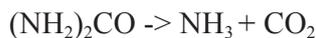
or



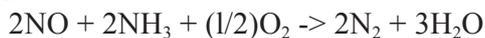
or



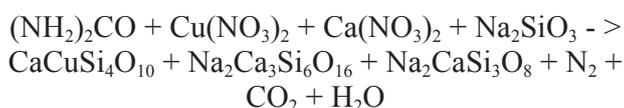
Urea decomposition reaction at high temperature [23]:



Reaction of ammonia occurs after decomposition/21/:



Overall reaction formulae is:



This reactions described mechanism of final measured products formation.

Semi-quantitive measurement results calculated as ratio of final products phases presented on Fig.

2. Ratio CaCuSi₄O₁₀/CuO and CaCuSi₄O₁₀/CuO is dropping with temperature (Fig. 3) because combustion temperature at preheating temperature higher than 700 °C is more than 1100 °C and Egyptian Blue decomposes at temperature above 1100 °C. Synthesis of Egyptian blue is possible approximately at 800–850 °C from Na₂CaSi₃O₈, Na₂Ca₃Si₆O₁₆ and CuO during sintering. That's why there is increasing of Egyptian blue during 2 h heating and decreasing of CuO concentration at 800 °C and 850 °C.

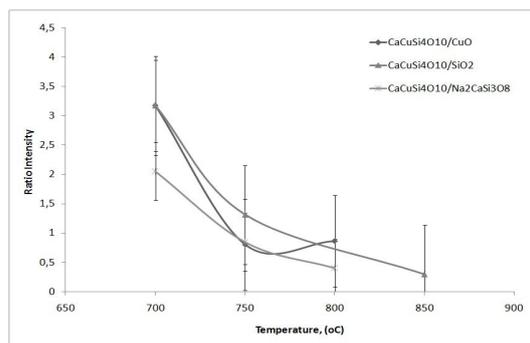


Fig. 3. The dependence of CaCuSi₄O₁₀/CuO, CaCuSi₄O₁₀/SiO₂ and CaCuSi₄O₁₀/Na₂CaSi₃O₈ ratio from preheating temperature.

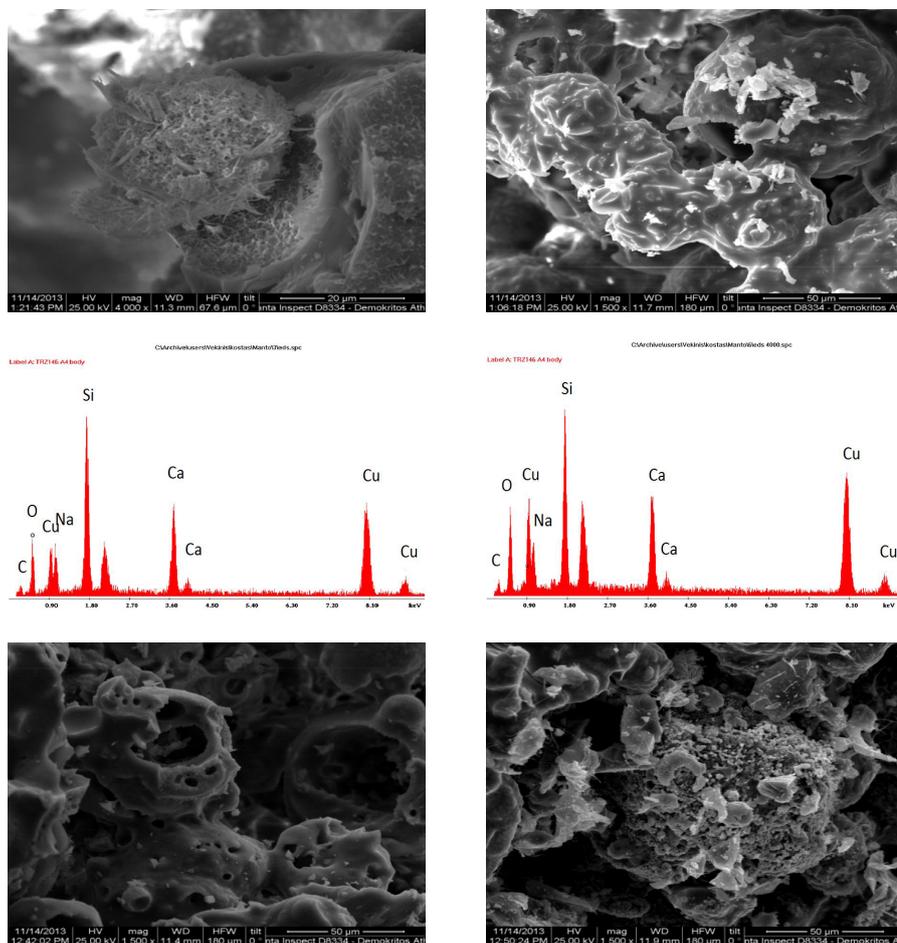


Fig. 4. SEM/EDX analysis of the Egyptian blue, microstructure of Egyptian blue pigment synthesized by SCS method.

From the Scanning Electron Microscope and EDX analysis was observed the microstructure and the composition of the produced pigments at magnifications of 1500x and 4000x (Fig. 4). It was found that synthesized $\text{CaCuSi}_4\text{O}_{10}$ has polycrystalline structure, in which crystallites are of fine or coarse texture. The microstructure of such aggregates composed of this polycrystalline material and silica granules which are retained with minor amounts of inter particle glass with following wollastonite based compounds: $\text{Na}_2\text{CaSi}_3\text{O}_8$ or $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$ (Fig. 4).

The Results of EDS analysis show variation of elements (Cu and Na) concentration (Fig. 4) in pigment, it show that during synthesis copper ions replace sodium ions in wollastonite base compounds $\text{Na}_2\text{CaSi}_3\text{O}_8$ or $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$ with origination of $\text{CaCuSi}_4\text{O}_{10}$.

Figure 5 show IR spectra of Egyptian blue pigment prepared by SCS at different temperatures.

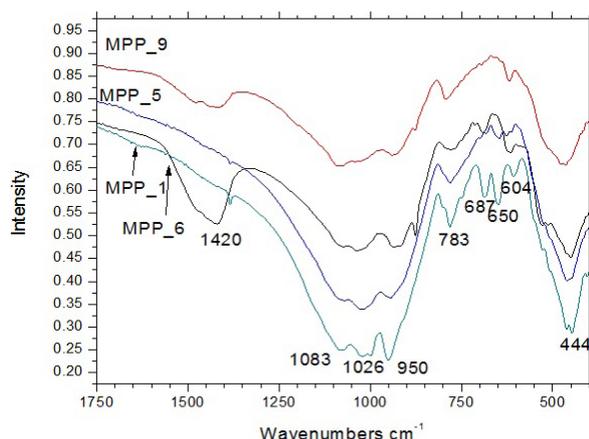


Fig. 5. IR spectra of Egyptian blue pigment prepared by SCS at different temperatures: MPP-1-850 °C, MPP-5-800 °C, MPP-9-750 °C, MPP-6-700 °C.

Infrared Spectra (region 400–1750 cm^{-1}) showing peaks around 470–505 cm^{-1} , 900–1100 cm^{-1} and 1360–1450 cm^{-1} . IR Spectra of the samples following thermal treatment at 700 °C and 750 °C (Fig. 5) displayed distinct infrared bands observed in the ranges at 1410–1360 cm^{-1} , related to NO_3^{2-} which was not recognized in other samples, this means that at temperatures 800–850 °C there is no nitrates in the final product, this also means that the reason of reduced yield of Egyptian blue at temperatures 700–750 °C connected with not complete reaction between nitrates and urea. It was found, that in the same samples (temperatures 700–750 °C) exist urea (1450–1520) cm^{-1} , this data also support conclusion that at those temperatures re-

action is not complete. The two bands observed in the ranges (485–505) cm^{-1} and at (670–680) cm^{-1} were attributed to CuO and those peaks exist at all temperatures except 850 °C, this data support data of XRD analysis, while the bands observed in the ranges (480–500) cm^{-1} and (810–820) cm^{-1} and (1110–1120) cm^{-1} are related to SiO_2 which exist in all samples.

The temperature has an important impact on the not only on emergence of the phases (Figs. 2 and 3) but also on the deformation of the crystal lattice (Fig. 6).

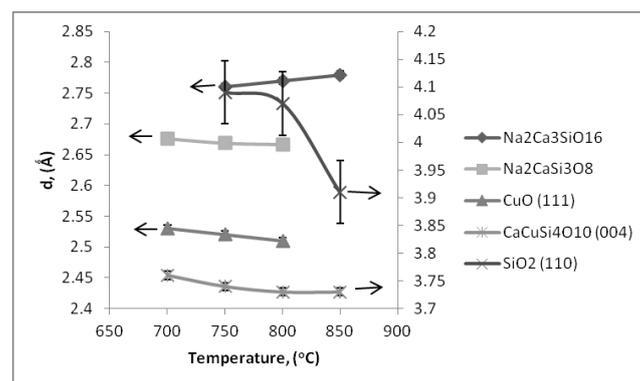


Fig. 6. Effect of temperature of initial charge treatment on the crystal lattice parameters.

According to data (Fig. 6) during heating SiO_2 change structure at 800 °C, it is followed by gradual preferential reorganization in crystal lattice. These dimensional changes can be attributed to thermal expansion and this could indicate a better arrangement of silicon and oxygen atoms within quartz structure. Slight changes of crystal lattice parameters of other phases during heating can be also explained by better arrangement of atoms within crystal lattice structure.

Figure 7 demonstrate influence of synthesis temperature on crystallite size of SCS pigment phases.

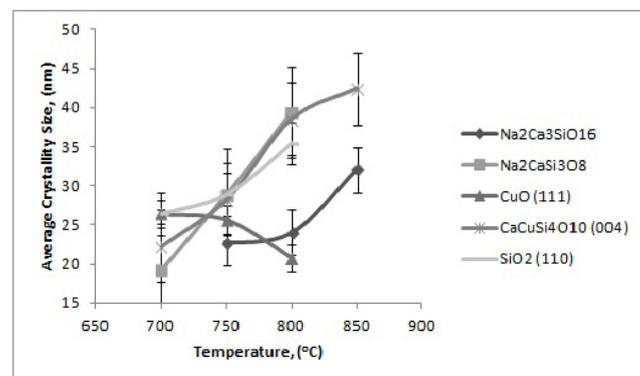


Fig. 7. Average crystallite size (nm) dependence from synthesis temperature.

Table 1

Egyptian blue pigment color characteristics produced by SCS at different preheating temperatures (initial composition: 25% Cu(NO₃)₂ + 24.6% Ca(NO₃)₂ + 50.4% Na₂SiO₃ + 3.6% H₂O + 40% Urea, 2 h heating)

Color characteristics	850 °C	800 °C	750 °C	700 °C
Hex triplet	#138CCO	#0B7F7F	#07666F	#07506F
RGB (r, g, b)	19, 140, 192	11, 127, 127	7, 102, 102	7, 80, 111
HSV	198°, 90%, 75%	180°, 91%, 50%	184°, 94%, 44%	198°, 94%, 44%
Color	Dark turquoise	Dark cyan	Teal	Midnight Blue

Increasing of synthesis temperature leads to sintering process and increasing of crystallite size. Crystallite size of all phases of SCS Egyptian blue pigment are variate from 10 to 42 nm. Crystallite size influences the color strength and shade, opacity, transparency. Increasing of pigment nanoparticles crystallite size lead to more light color (Table 1).

Increasing preheating temperature lead to increasing of Egyptian blue concentration and pigment became dark turquoise-classic Egyptian blue color (Table 1). The shade of Egyptian blue was related to the coarseness and fineness of Egyptian blue as it was determined by the degree of aggregation of the Egyptian blue crystals.

4. Conclusion

Egyptian blue nanoparticles pigment was successfully synthesized by SCS method. The size of the particles was found to increase at increasing of preheating and sintering temperature. On the other hand, raising temperature increased concentration of Egyptian blue in the final product. This led to color changing. The shade of Egyptian blue was also related to the coarseness and fineness of pigment as it was determined by the degree of aggregation of the Egyptian blue crystals. It was found, that Egyptian blue formation depends from SCS and sintering conditions: at 700–750 °C reaction is not complete, at 800–850 °C is observed decreasing of the yield during SCS due to combustion temperatures above 1050 °C (in this conditions pigment become unstable), but because of additional sintering at 800–850 °C for 2 h yield of Egyptian blue increased, due to replacing sodium ions with copper ions in the compounds Na₂CaSi₃O₈, Na₂Ca₃Si₆O₁₆ produced by SCS. Thus, at 850 °C was observed the highest percentage of the Egyptian blue.

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