The use of mechanochemical activation for the synthesis of garnet-based pigments

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Abstract. Green pigments based on uvarovite $\text{Ca}_3\text{Cr}_2[\text{SiO}_4]\_3$ were obtained from cheap silica-containing materials of the Siberian region by high-temperature solid-phase synthesis with the use of mechanical activation of an initial mixture. The chemical composition of quartz sand and marshallite, the main initial components of pigments, is determined using an optical emission spectrometer with inductively coupled plasma (iCAP 6300 Duo, Thermo Scientific). The structure and phase composition of initial materials and reaction products were analyzed by X-ray diffraction (DRON-UM1 diffractometer, filtered CuKa-radiation), IR spectroscopy (Nicolet 5700 FTIR spectrometer), and scanning electron microscopy (Philips SEM 515). Calcium carbonate is shown to decompose during mechanochemical activation. The reactions occurring during the synthesis of pigments were studied using a thermal analyzer (SDT Q600) in the temperature range of 25-1200°C at a heating rate of 20 deg/min. Mechanical activation of initial components in a planetary mill M3 with an acceleration of 45 g for 300 s leads to a decrease in the synthesis temperature by 200°C and increases the degree of conversion of the final products.

1. Introduction

Pigments with a garnet structure refer to heat-resistant inorganic pigments. They have a bright colour, increased heat-resistance, high covering ability and can be used for colouration of ceramic, porcelain and plastic products [1].

The general chemical formula of garnets is as follows: $\text{R}^{2+}_3\text{R}^{3+}_2[\text{SiO}_4]_3$, где $\text{R}^{2+} = \text{Mg}, \text{Fe}, \text{Mn}, \text{Ca}$; $\text{R}^{3+} = \text{Al}, \text{Fe}, \text{Cr}$. Colouration depends on the constituent elements of mineral and varies in the wide range of colours, including blue [2-5]. The cubic structure of garnet is stable in a wide range of substitutions of both divalent and trivalent cations and is represented by a skeleton of interconnected Si-tetrahedra and R$^{3+}$ octahedra, in the cavities of which R$^{2+}$ ions are located. $\text{Ca}_3\text{Cr}_2[\text{SiO}_4]_3$ uvarovite, emerald green calcium-chromium silicate, can be marked among garnets. Its colouration is due to the presence of Cr$^{3+}$ chromophore, and it is heat-resistant up to 1370°C [6]. As a rule, synthetic garnets are obtained by solid-phase synthesis at high temperatures of 1200-1250°C from chemically pure reagents or wastes [1, 6].

In this work inorganic pigments based on uvarovite $\text{Ca}_3\text{Cr}_2[\text{SiO}_4]_3$ were obtained by solid-phase synthesis using sand or marshallite as the main component. The use of mechanical activation (MA) of initial reagents accelerated the solid-phase synthesis process and increased the conversion degree of reactions, which made it possible to obtain homogeneous products at lower temperatures. However, the processes associated with their obtaining and the behavior of colour phases after thermal and
mechanoochemical treatments have not been fully studied so far. So, the purpose of this work is to obtain green pigments using sand and marshallit and study the effect of mechanical activation and heat treatment on the phase composition and structure of the uvarovite-based pigment.

2. Materials and procedure

Natural materials, such as marshallit, sand, natural chalk, and Cr$_2$O$_3$ pure chromium oxide were used as initial components. The synthesis was conducted by the traditional ceramic procedure in the EKPS-50 furnace at different temperatures and time. The mixture of the initial components was mechanically activated in a M3 planetary mill with an acceleration of 45g for 30-300 sec. The mass ratio of the balls to the mixture was 5:1.

The thermal analysis of the initial mixture subjected to mechanical activation and without it was conducted using a thermal analyzer SDTQ600 with a heating rate of 20 deg/min in the temperature range of 25-1200°C. The microstructure of the pigments was investigated by scanning electron microscopy (PhilipsSEM 515). The initial materials and the final product was studied by X-ray diffraction (DRON-UM1 diffractometer, filtered CuKα-radiation) and IR spectroscopy (Nicolet 5700 FTIR spectrometer with a diffuse reflection in KBr). The chemical composition of the minerals was determined on the optical emission spectrometer with inductively coupled plasma (iCAP 6300 Duo, ThermoScientific). The quantitative analysis of the products was carried out using the Match code and the PDF-2 database.

3. Results and discussion

To reduce the cost of pigments, available natural materials, in particular marshallit (SiO$_2$), sand (SiO$_2$) of the Siberian region and natural chalk (CaCO$_3$) were used as initial materials.

The chemical composition of the silica-containing minerals used for the synthesis of pigments was determined on an iCAP 6300 Duo spectrometer and given in Table 1. As can be seen, quartz sand contains the higher amount of iron as an impurity compared to marshallit, as a result it has a beige colour.

| Mineral       | Content of oxides, wt.% | a$\Delta$m_{calc}, % |
|---------------|-------------------------|----------------------|
|               | SiO$_2$  | Al$_2$O$_3$ | CaO | MgO | Fe$_2$O$_3$ | TiO$_2$ | R$_2$O |
| Quartz sand   | 88.8     | 4.7         | 0.6 | 0.3 | 0.9         | 0.2     | 2.9    | 1.6 |
| Marshallit    | 96.3     | 1.5         | 1.0 | 0.4 | 0.1         | traces  | 0.3    | 0.4 |

a$\Delta$m_{calc} is mass loss during calcination.

A feature of the synthesis of pigments with a garnet structure are high temperatures (about 1200÷1250°C) and long keeping [1]. The mechanical activation of the initial mixture provides a high degree of dispersion and homogeneity of the mixture of initial reagents in combination with the accumulation of structural defects caused by mechanical processing, as well as leads to a decrease in the synthesis temperature, ensuring the completeness of reactions. Figure 1 shows the TG, DTA curves of the thermal analysis of the CaO-Cr$_2$O$_3$-SiO$_2$ initial system consisting of a mixture of CaCO$_3$, Cr$_2$O$_3$, SiO$_2$ (marshallit), using mechanical activation and without it.

At a temperature of 131.5°C, a slight endo-effect is observed on the DTA curve of the initial mixture without MA due to the removal of water contained in natural minerals (chalk, marshallit). In both cases, $\alpha$-quartz $\rightarrow$ $\beta$-quartz phase transition is detected at 569.4°C [7]. The endo-effect with a mass loss of the mixture at 753°C is associated with the decomposition of calcium carbonate and the formation of light green CaCr$_2$O$_4$ [8].
CaCO$_3$+Cr$_2$O$_3$=CaCr$_2$O$_4$+CO$_2$↑  \hfill (1)

The increase in temperature (above 800 °C) leads to the increase in mass and the formation of CaCrO$_4$, yellow calcium chromate that is stable to a temperature of 1022 °C [8].

\[ 2\text{CaCr}_2\text{O}_4 + 2\text{CaO} + 3\text{O}_2 = 4\text{CaCr}_2\text{O}_4 \] \hfill (2)

Figure 1. TG, DTA curves of the thermal analysis of the initial CaO-Cr$_2$O$_3$-SiO$_2$ system consisting of a mixture of CaCO$_3$, Cr$_2$O$_3$, SiO$_2$, using mechanical activation in the M3 planetary mill for 300 sec (dotted line) and without it (solid line).

Above this temperature, CaCrO$_4$ and residual CaCO$_3$ decompose, and Ca$_3$Cr$_2$(SiO$_4$)$_3$, with an impurity of various calcium chromosilicates is formed. The pigment acquires a bright green colour.

CaCrO$_4$ calcium chromate decomposes with loss of mass according to the reactions as follows [8]:

\[ 4\text{CaCr}_2\text{O}_4 \rightarrow 2\text{CaO} + 2\text{CaCr}_2\text{O}_4 + 3\text{O}_2 \] \hfill (3)

\[ 6\text{CaO} + 6\text{CaCr}_2\text{O}_4 = 2(9\text{CaO}·4\text{CrO}_3·\text{Cr}_2\text{O}_3) + 3\text{O}_2 \] \hfill (4)

During the formation of chromato-chromite calcium (9CaO·4CrO$_3$·Cr$_2$O$_3$), oxygen is released at a temperature of ~1000°C.

Due to the mechanical activation of the initial mixture, the processes associated with the synthesis of pigments proceed at lower temperatures. This fact is demonstrated on the DTA curve (for the initial mixture after mechanical activation).

IR spectroscopic analysis of the initial mixture with the use of mechanical activation for 30, 60, 120 and 300 s and without it showed that even by 30 s of MA there was a decrease in the intensity of the absorption bands at 1793.4 cm$^{-1}$, 1445.8 cm$^{-1}$ and 877.9 cm$^{-1}$, corresponding to calcium carbonate, which indicates its decomposition (figure 2). The appearance of a straight line at ~850 cm$^{-1}$ and the shift of the absorption bands at 628.5 cm$^{-1}$ to the high-frequency region indicates the formation of chromites during the process of MA [9]. Depending on the synthesis temperature, it is possible to obtain the final product in different colours. Thus, at 750°C, a bright green product (kiwi colour) is formed, which is associated with the synthesis of CaCrO$_4$ spinel-type calcium chromite. The increase in the temperature to 800÷900°C changes the colour to greenish-yellow due to the formation of CaCrO$_4$, yellow calcium chromate. Along with chromocalcium compounds, according to X-ray phase
analysis, the products contain green silicates and chromosilicates of calcium (\(\text{Ca}_3\text{Si}_2\text{O}_7\), \(\text{CaCrSi}_3\text{O}_{10}\), \(\text{Ca}_5\text{Cr}_2\text{SiO}_{12}\)).

![Graph of IR spectra](image1)

**Figure 2.** IR spectra of the initial bright green mixtures subjected to mechanical activation for 30 sec (1), 60 sec (2), 120 sec (3) and 300 sec (4) and without it (5).

The synthesis conducted at \(\sim 1000^\circ\text{C}\) with the use of mechanical activation of the initial mixture for 300 s leads to the formation of emerald green uvarovite \(\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3\). The iron impurities contained in quartz sand provide the pigment with a lighter shade. As can be seen (figure 3), the pigments consist mainly of two phases: the main phase is uvarovite \(\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3\) and an impurity of \(\text{SiO}_2\). At the same time, the pigment synthesized from \(\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3\) marshallit contains a smaller amount of quartz. \(\text{CaCrO}_4\) and calcium chromosilicates (\(\text{CaCrSi}_3\text{O}_{10}\), \(\text{Ca}_5\text{Cr}_2\text{SiO}_{12}\)) are determined by the noise level.

![Graph of X-ray diffraction patterns](image2)

**Figure 3.** X-ray diffraction patterns of garnet-based pigment synthesized from sand and marshallit, where (1) \(\text{SiO}_2\), (2) uvarovite \(\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3\).

A quantitative analysis of the products carried out using the Match code and the PDF-2 database showed that sand-based pigments synthesized contained 76 wt.% uvarovite, and the pigments obtained from sand contained 90 wt.% uvarovite (MA=300 s). The synthesis temperature reduces by 200 °C and is \(\sim 1000^\circ\text{C}\), the keeping time is 1 hour. The same amount of the uvarovite phase in marshallit is
formed due to step heating $T_c=750^\circ C (2\ h)+1050^\circ C (0.1\ h)$ with the use of mechanical activation of the initial mixture for 30 s. Keeping at $750^\circ C$ leads to the complete decomposition of $\text{CaCO}_3$ with the formation of calcium chromite, which simplifies the further synthesis of uvarovite.

Figure 4 shows the microstructure of a garnet-type pigment, the initial components of which consist of a mixture of $\text{CaCO}_3$, $\text{Cr}_2\text{O}_3$ and sand. As can be seen, the pigment has a fine-grained structure with a grain size of $\sim \mu m$.

![Figure 4. Microstructure of a garnet-type pigment based on $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ uvarovite synthesized from Tomsk sand.](image)

4. Conclusion

Green pigments based on uvarovite $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ were obtained from cheap silica-containing materials of the Siberian region by high-temperature solid-phase synthesis with the use of mechanical activation of an initial mixture. It is established that MA in the M3 planetary mill with an acceleration of 45 g leads to the decomposition of $\text{CaCO}_3$ and the formation of $\text{CaCr}_2\text{O}_4$ calcium chromite. The synthesis temperature decreases by 200°C. Mechanical activation of the initial mixture for 300 s increases the degree of conversion of final products and the proportion of colour phase with a garnet structure. Due to step heating, the phase of uvarovite is actively formed even after mechanical activation for 30 s and short high-temperature keeping (0.1 h).

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