



## Preparation and characterization of chrome doped sphene pigments prepared via precursor mechanochemical activation



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### ABSTRACT

Mechanical activation of precursors has been used for the preparation of Cr-doped sphene ceramic pigments ( $\text{CaTi}_{1-y}\text{Cr}_y\text{SiO}_5$ ). Ceramic material has been prepared from a powder mixture of  $\text{CaCO}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  using vibro-milling for homogenization and activation of precursors. The mechanochemical process initially yielded amorphous powders, which on further calcination, crystallized to yield Cr-doped sphene ceramic pigment. Phase evolution in  $\text{CaTi}_{1-y}\text{Cr}_y\text{SiO}_5$  composition with thermal treatment was investigated by X-ray powder diffraction (XRPD). Texture properties and particle size distribution were analyzed by scanning electron microscopy (SEM) and laser diffraction, respectively. UV/Vis reflectance spectra are used to determinate the behavior of the chromium ion. The color efficiency of pigments was evaluated by colorimetric analysis (CIE  $L^* a^* b$  system). Photoluminescence measurements were also performed.

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## 1. Introduction

Inorganic pigments are used for the mass coloration of many materials including glazes and ceramic bodies [1]. Ceramic pigments have been used in the industry because of their high temperature resistance, chemical stability (low corrosion) and sufficient optical properties [2]. With a few exceptions, the majority of the ceramic pigments are based on inorganic oxides. Many attempts have been made to extend the range of ceramic pigments [3–5]. Sphene, up to now is still unused as a ceramic pigment, unlike his analogue malayaite  $\text{CaSnSiO}_5$ . Cr-doped malayaite (topologically identical to sphene) develops a pink color [6], whereas Cr-doped sphene possesses reddish brown hues [7,8] and can replace other brown pigments.

Sphene or titanite belongs to the group of nesosilicate minerals with monoclinic symmetry. It can crystallize both as primary (space group  $A2/a$ ) and lower-T phase (space group  $P2_1/a$ ). The ideal chemical formula of sphene can be written as  $\text{CaTiSiO}_5$  or  $\text{CaTiO}(\text{SiO}_4)$  [9]. Significant substitutions within the structure, in both cation and anion sites, allow to prepare industrial pigments [10–12]. It was noted that all the atoms of titanium in octahedral chain moved in the same direction along the axis  $a$ . These atoms are moved out from their geometric center in octahedrons, which

is reflected in structure geometry i.e. longer and shorter Ti–O bonds [13]. Because of the distorted  $\text{TiO}_6$  octahedra and consequent low point symmetry, sphene is desirable to develop an intense coloration [6]. It can also be used as luminescent material [14] since it is possible to incorporate a variety of elements into its crystal lattice.

Many different methods such as sol–gel [15], coprecipitation [15], combustion [16], spray pyrolysis [8], freeze-drying [17] and hydrothermal methods have been used in order to obtain ideal powder that would consist of approximately spherical particles with uniform size and distribution.

In this paper we describe a method for the preparation of pigment with Cr-doped sphene composition using mechanochemical activation of precursors prior to synthesis ceramic pigment [18]. So far, many sphene pigments are synthesized by this method using ball milling technology [5,19–22]. In this study, vibratory mills are used. They are classed with grinding devices operating via impact and attrition. In such mills the impact is produced by the grinding body sliding over the material being ground or rotating around some axis. Mechanically induced violation of the mineral grain structure is accompanied by reduction of the mineral particles size [23] which is highly desirable for application in the ceramic pigments [24]. Several samples with sphene composition and different Cr amount were synthesized and thermally treated. Also, pigments were characterized morphologically, crystallographically and optically.

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## 2. Experimental methods

### 2.1. Powder preparation

Reactants used in the synthesis are commercially obtained powders: TiO<sub>2</sub> (Lab. Art. 808 E. Merck), SiO<sub>2</sub> (ASP-K-amorphous, Prahovo), CaCO<sub>3</sub> (pro analysis, 11490, Kemika, Zagreb) and Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Aldrich, 99.9% purity). All precursors have been dried at 105 °C for 24 h and storage in an exsiccator to avoid atmospheric moisture before weighing. Six samples were prepared from stoichiometric amounts of these powders in order to obtain 5 g of Cr-doped sphene (CaTi<sub>1-x</sub>Cr<sub>x</sub>SiO<sub>5</sub>). The powder mixtures were homogenized in the vibratory mill (Fritsch Pulverisette Analysette Laborette, type 09 003, No. 155, 380 volt). The Vibratory Pulverizer uses ring ( $\phi = 5.3$  cm,  $h = 4.3$  cm) and a disk ( $\phi = 10.3$  cm,  $h = 4.3$  cm) inside a hard-metal tungsten carbide grinding bowl ( $\phi = 13$  cm,  $h = 6.3$  cm). Volume of the container is 100 ml with  $m = 3200$  g. The device can operate at two speeds of vibration: 750 min<sup>-1</sup> and 1000 min<sup>-1</sup>. Samples were ground for 30 min in air atmosphere with speed of 750 min<sup>-1</sup>.

Six pellets were made from each sample for a different amount of Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O ( $\phi = 8$  mm,  $h = 5$  mm). They were obtained by hydraulic pre-pressing under the pressure of 100 MPa. Sintering of compacted powders was carried out at 1200 °C in the air at a heating rate of 10 °C/min and a soaking period of 2 h in alumina crucibles.

### 2.2. Characterization

All of the powders were characterized at room temperature by X-ray powder diffraction (XRPD) using Ultima IV Rigaku diffractometer, equipped with Cu K $\alpha_{1,2}$  radiation, using a generator voltage (40.0 kV) and a generator current (40.0 mA). The range of 10–90° 2 $\theta$  was used for all powders in a continuous scan mode with a scanning step size of 0.02° and at a scan rate of 2°/min.

The sintered pellets were polished and thermally etched at temperature of 1150 °C for 30 min. Microstructure and chemical composition were investigated with C (graphite) coating using a JEOL JSM-6610LV scanning electron microscope (SEM) connected with an INCA energy-dispersion X-ray analysis unit (EDX). An acceleration voltage of 20 kV was used.

Diffuse spectral reflectance measurements were done in the spectral range 350–800 nm, on the Thermo Evolution 600 spectrometer equipped with an integrating sphere, using BaSO<sub>4</sub> as a blank.

Fluorescence excitation and emission spectra are measured were performed on a Fluorolog-3 Model FL3-221 spectrofluorometer (Horiba JobinYvon) utilizing a 450-W Xenon lamp as the excitation source and a TBX detector.

The color characteristics of specimens were calculated according to the CIE  $L^* a^* b^*$  (1976) standard, using illuminant C spectral energy distribution. In this system,  $L^*$  is the color lightness ( $L^* = 0$  for black and  $L^* = 100$  for white),  $a^*$  is the green (–)/red (+) axis, and  $b^*$  is the blue (–)/yellow (+) axis.

## 3. Results and discussion

The compositions of the six precursors were prepared with the stoichiometry of sphene and different Cr content (CaTi<sub>1-x</sub>Cr<sub>x</sub>SiO<sub>5</sub>, Cr/Ti atomic ratio = 0.03, 0.05, 0.1, 0.15, 0.35 and 0.5). The best experimental condition for preparing sphene for further calcination and sintering process was grinding time of 30 min in vibratory mill and the highest achieved density was obtained at 1200 °C [18]. These conditions were used for preparing sphene doped with chrome.

The XRPD patterns of all the samples that were mechanochemically activated 30 min (Fig. 1) depict the formation of sphene (CaTiSiO<sub>5</sub>) as a principle crystalline phase at 1200 °C. The main reflections in these patterns are observed at 2 $\theta$  of about 17°, 27°, 29°, and 34°, which is typical for the sphene structure. Minor amount of perovskite (CaTiO<sub>3</sub>), a secondary phase, was detected. Only in samples with Cr/Ti atomic ratio = 0.03, 0.05, 0.35 and 0.5 small amount of coesite (SiO<sub>2</sub>) was detected. No other SiO<sub>2</sub> phase mach these reflections on the diagram. The third phase, coesite (SiO<sub>2</sub>), was noticed also during XRPD measurements and in the Rietveld refinement the lattice parameters, atomic coordinates, and microstructural parameters simultaneously were refined [18]. All the structure information was taken from American Mineralogist Crystal Data Structure Base (AMCDSB) [25].

All samples developed similar structural and morphological characteristics on thermal treatments. The microstructure of the sphene doped with Cr with grinding time 30 min heated at

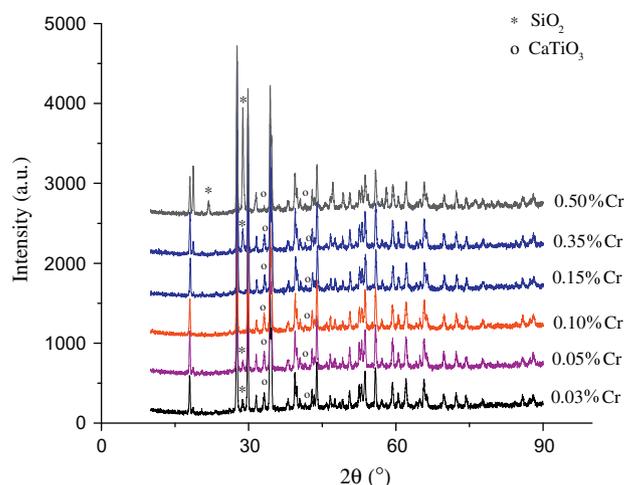


Fig. 1. X-ray diffraction patterns of sphene doped with Cr (30 min grinding) after heating at 1200 °C. Symbols: ●—CaTiO<sub>3</sub>, \*—SiO<sub>2</sub>. The sphene peaks have not been labeled.

1200 °C is shown in Fig. 2a–d. The average particle size estimated from SEM images is around 1  $\mu$ m, which is desirable for application [24]. The micrographs revealed the dense nature of the compact material sintered at 1200 °C with the irregular shaped and elongated grains. As Fig. 2a reveals, vibratory mills are highly efficient as regards achievement of the desired particle size of the sphene particles (<10  $\mu$ m) [26]. The order of element abundance is Ca, Ti, Si and O suggesting major presence of a sphene in investigating samples. Presence of Ca, Si, Ti and Cr were evident in investigating samples, as indicated by the EDX analysis (Fig. 2d).

All the pigments were analyzed by UV–Vis spectroscopy in order to study the surrounding of the Cr. The absorption spectra corresponding to the synthesized samples are presented in Fig. 3. Judging by the weak but visible absorption maxima, Cr enters a lattice site in sphene, increasing the overall level of absorption. The change in relative intensities of the absorption maxima produces a shift in color tone. In general, the spectra present similar features, and the intensity of the absorption peaks increase with chromium concentration. The visible region is dominated by a broad band centered around 500 nm and can be explained by the presence of Cr<sup>4+</sup>. The d–d electron transitions of Cr<sup>4+</sup> are hosted in distorted octahedral coordination [20]. The band at 570 nm is attributed to the <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1g</sub>(F) and <sup>4</sup>A<sub>2g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(F) transitions of Cr<sup>3+</sup> in octahedral sites [27]. For sixfold coordination, the chromium ion (Cr<sup>3+</sup>) has an ionic radius (0.615 Å) and it is similar with the Ti ion (0.605 Å), finds itself within distorted octahedral [28]. Therefore the ligands along the *a*-axis are more distant from the central ion in comparison with the others. Consequently, splitting of the d orbitals of the Cr<sup>3+</sup> ion and the transition of energy from the higher energy level to lower energy level gives rise to the color. When the central ion, inside an octahedrally coordinated cage is chromium, the field is strong enough to allow absorption in the visible spectrum, for wavelengths located in the blue and green region.

Color changing is very intensive with the increase of Cr content from 0.03% to 0.5%. It is obvious from the corresponding  $L^* a^* b^*$  coordinates (Table 1). For the prepared sample with 0.05% Cr,  $a^*$  (3.568), relatively high  $b^*$  (6.473) and  $L^*$  (83.316) were detected. On further increasing Cr concentration,  $L^*$  decreases until it reaches 0.15% Cr. Therefore, the color shifted from light pink–brown toward darker pink–brown hue (increasing  $a^*$ ) and becoming more saturated (decreasing  $L^*$ ) with the increasing Cr concentration. Above 0.15% Cr,  $L^*$  begins to increase. The limit is 0.15% Cr, after  $a^*$  has started to decrease. Progressive decrease (from 83.316 to 61.624) of luminosity ( $L^*$ ), i.e. further increase in the color intensity

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