



# Chromium-doped calcium zirconate – A potential red shade pigment: Preparation, characterization and testing



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## ABSTRACT

Chromium doping of calcium zirconate,  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  ( $x = 0-0.07$ ), leads to red shade pigments. XRD analysis confirmed that  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  solid solution is the only crystalline phase present in the samples annealed at 1400 °C. The substitution of  $\text{Zr}^{4+}$  by  $\text{Cr}^{4+}$  causes a progressive decrease of the unit cell volume, because  $\text{Zr}^{4+}$  has an ionic radius larger than  $\text{Cr}^{4+}$ . The  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  crystallite size decreases as the substitution degree increases, from 64 nm ( $x = 0$ ) to 46 nm ( $x = 0.07$ ). The diffuse reflectance spectra of  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  pigments show a broad absorption band between 400 and 650 nm.  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  pigments are located in the red-yellow area of the CIEL\*a\*b\* color space. The proportion of red ranges between 16.7 and 19.0, whilst the proportion of yellow varies between 6.4 and 8.2. The brightness of the pigments decreases as the chromium proportion increases. Testing the  $\text{CaZr}_{0.93}\text{Cr}_{0.07}\text{O}_3$  pigment in coloring a semi-transparent enamel showed that the pigment is dissolved by the molten glass. At the same time,  $\text{Cr}^{4+}$  is reduced to  $\text{Cr}^{3+}$ , which is responsible for the green color of the enamel.

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## 1. Introduction

Ceramic pigments also known as thermoresistant pigments are colored inorganic compounds, which are able to keep their coloring properties even when subjected to high temperatures and chemically aggressive conditions, such are enamels and glazes.

Obtaining various red tints proved to be a delicate issue in the field of ceramic pigments fabrication, since there are not many structures and chromophores to provide quality coloring features and withstand the harsh firing conditions. Except for the pigments based on Cd(S,Se), most of the red hue pigments that are currently used in the industry have either  $\text{Cr}^{3+}$  and/or  $\text{Cr}^{4+}$  chromophore [1] included in various crystalline networks.

Recent research has focused on developing new chromium  $\text{Cr}^{3+}$ / $\text{Cr}^{4+}$ -based pink-red pigments using various host crystalline networks to ensure thermal and chemical stability, such are:  $\text{Al}_2\text{O}_3$  [2],  $\text{SnO}_2$  [3,4],  $\text{TiO}_2$  [5–9],  $\text{ZnAl}_2\text{O}_4$  [10–12],  $\text{YAlO}_3$  [13,14],  $\text{LaAlO}_3$ ,  $\text{NdAlO}_3$  [2],  $\text{CaYAlO}_4$  [15],  $\text{CaSnSiO}_5$  [16–20],  $\text{Y}_2\text{Sn}_2\text{O}_7$  [21],  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  [22].

While the chromium-doped calcium titanate pigments have been the subject of many papers [23–26], little attention has been paid to the effects of chromium-doping of calcium zirconate, particularly its effects on the crystal structure and the optical properties.

In an attempt to prepare  $\text{Ca}(\text{Cr}_x\text{Zr}_{1-x})\text{O}_3$  solid solutions ( $x = 0.025, 0.05, 0.1$  and  $0.2$ ) at 1000 °C, Gargori et al. [24] obtained a mixture of perovskite ( $\text{CaZrO}_3$ ), monoclinic and cubic zirconia ( $\text{ZrO}_2$ ). According to the same authors, the  $\text{Ca}(\text{Cr}_x\text{Zr}_{1-x})\text{O}_3$  solid solution was not reached completely and the obtained samples were not stable in glazes.

The present paper discusses the preparation, characterization and testing of a red shade pigment, based on chromium-doped calcium zirconate. This pigment derives from  $\text{CaZrO}_3$  belonging to the orthorhombic perovskites group, by the partial substitution of zirconium by chromium,  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  ( $x = 0-0.07$ ). Ideally, the perovskite structure has a cubic symmetry and the general formula  $\text{ABO}_3$ . The A-site ions have larger ionic radius and are located on the corners of the lattice, whilst the B-site ions have smaller ionic radius and are located on the center of the lattice. In the case of orthorhombic  $\text{CaZrO}_3$ ,  $\text{Zr}^{4+}$  cations are octahedrally coordinated whilst  $\text{Ca}^{2+}$  cations are 8-fold coordinated [27–29].  $\text{CaZrO}_3$  was chosen as a potential candidate for host crystalline network due to its high melting point [27,28].

## 2. Experimental section

In order to obtain the red-shade pigments based on  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$ , the ceramic method was used based on annealing mechanical mixtures of oxides and salts. The following raw materials were used in order to achieve  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  ( $x = 0-0.07$ ) formation:  $\text{CaCO}_3$  (Sikal Trading),  $\text{ZrO}_2$  (Cerasil) and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

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(Merck). The samples were denoted as follows: 0 ( $x = 0$ ), 1 ( $x = 0.01$ ), 3 ( $x = 0.03$ ), 5 ( $x = 0.05$ ) and 7 ( $x = 0.07$ ). The raw materials were manually wet homogenized in a mortar with pestle. The water was subsequently evaporated from the mixtures by heating at 110 °C in a drying oven. After grinding, the raw materials mixtures were annealed at 1400 °C for 2 h. The obtained pigments were manually ground, rinsed with hot distilled water, dried and then characterized.

The  $\text{CaZr}_{0.93}\text{Cr}_{0.07}\text{O}_3$  pigment was tested in coloring a semi-transparent enamel. For this purpose, a slurry consisting of enamel frit (52.0%  $\text{SiO}_2$ , 6.7%  $\text{Al}_2\text{O}_3$ , 18.3%  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , 15.4%  $\text{B}_2\text{O}_3$ , 1.9%  $\text{P}_2\text{O}_5$ , 1.9%  $\text{MgO}$ , 3.8%  $\text{CaF}_2$ ) with 5% wt. kaolin addition and 10% wt. pigment was prepared by wet ball milling and applied onto a metallic substrate, which was already covered by a fired ground enamel. After drying, the test enamel (named sample E) was fired at 820 °C for 5 min.

The heating behavior of the raw materials mixtures was investigated by means of thermal analysis using a Netzsch 449 C instrument. The TG-DTA data were recorded in static air atmosphere, at a heating rate of 10 °C/min, in Pt crucibles. The phase composition of the annealed samples was established via X-ray diffraction using a Rigaku Ultima IV instrument,  $\text{CuK}\alpha$  radiation at 40 kV and 40 mA. The crystallite size and unit cell parameters (unit cell volume) were calculated based on the hkl peaks 101 and 202, using the instrument-integrated PDXL 2.0 software (the Scherrer method). The instrumental broadening was subtracting from the measured XRD patterns using a Si standard.

The color of the samples, including the  $\text{CIEL}^*a^*b^*$  parameters, was studied by diffuse reflectance spectrometry using a Varian Cary 300 Bio UV-VIS instrument and  $\text{D}_{65}$  illuminant, at an observer's angle of 10°. Particle morphology was investigated by scanning electron microscopy using a FEI Quanta FEG 250 instrument.

### 3. Results and discussion

Thermal analysis of the raw material mixture (sample 0) undergoes an endothermic process at 829 °C (Fig. 1). The process is accompanied by a mass loss of 19.78%, which may be assigned to  $\text{CaCO}_3$  decomposition reaction. As a matter of fact, the actual mass loss of the sample (19.78%) complies with the theoretical mass loss

of the sample (19.72%). Except for the endothermic effect assigned to  $\text{CaCO}_3$  decomposition, the DTA curve shows no other thermal effects that could be attributed to the formation of calcium zirconate,  $\text{CaZrO}_3$ . This behavior can be explained by the overlap of the  $\text{CaCO}_3$  decomposition and  $\text{CaZrO}_3$  formation processes, so that the endothermic effect associated with the thermal decomposition of  $\text{CaCO}_3$  masks the thermic effect associated with the  $\text{CaZrO}_3$  crystallization [30,31].

The XRD patterns confirm that  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  solid solution is the only crystalline phase present within all the samples (Fig. 2), which means that  $\text{Cr}^{4+}$  uptake within the calcium zirconate structure occurs over the entire range of investigated compositions ( $x = 0-0.07$ ). As the amount of chromium entering the  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  structure increases, there is a slight shift of the peak position towards higher angles (Fig. 2 – detail).

The unit cell volume of sample 0,  $\text{CaZrO}_3$  (257.70 Å<sup>3</sup>) is close to the value of  $\text{CaZrO}_3$  (257.86 Å<sup>3</sup>) indicated in the PDF file 350790. At the same time, one may notice that the unit cell volume of  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  samples containing chromium decreases progressively with the increase of the substitution degree,  $x$  (Fig. 3). This evolution can be explained by the fact that the ionic radius of 6-fold coordinated  $\text{Zr}^{4+}$  (0.72 Å) is larger than the ionic radius of 6-fold coordinated  $\text{Cr}^{4+}$  (0.55 Å) [32]. The large difference in ionic size between  $\text{Cr}^{4+}$  and  $\text{Zr}^{4+}$  makes it possible to detect small variations of the unit cell volume even for low doping levels:  $x = 0-0.07$ . The substitution of a larger cation ( $\text{Zr}^{4+}$ ) by a smaller one ( $\text{Cr}^{4+}$ ) is therefore responsible for the shrinkage of the  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  unit cell volume (Fig. 3).

The average crystallite size of  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  solid solutions seems to be dependent on the substitution degree (Fig. 4). As the proportion of  $\text{Cr}^{4+}$  replacing  $\text{Zr}^{4+}$  increases from sample 0 ( $\text{CaZrO}_3$ ) to sample 7 ( $\text{CaZr}_{0.93}\text{Cr}_{0.07}\text{O}_3$ ), the crystallite size decreases from 64 to 46 nm. This behavior suggests that the increase of  $\text{Cr}^{4+}$  uptake within the calcium zirconate structure hinders the crystallites growth.

The color of  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  samples annealed at 1400 °C for 2 h is closely related to their stoichiometry (Fig. 5). Whilst the chromium-free sample is white (sample 0), the chromium-doped calcium

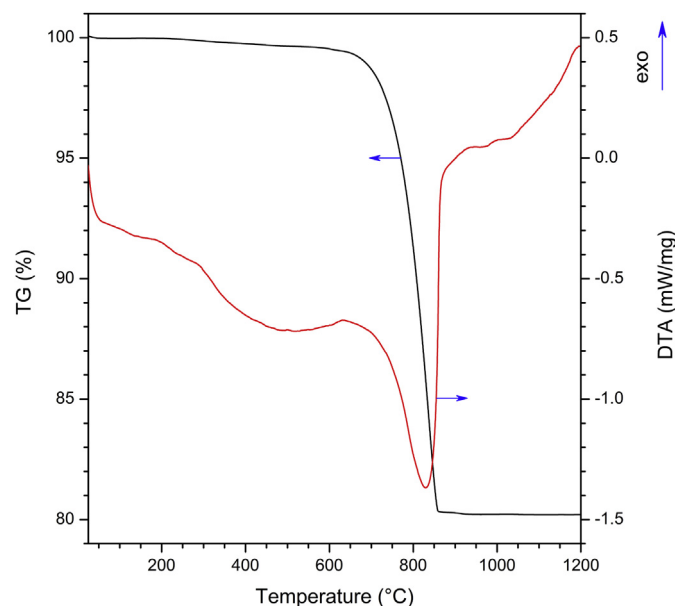


Fig. 1. Thermal analysis of the precursor mixture consisting of  $\text{CaCO}_3$  and  $\text{ZrO}_2$  (sample 0).

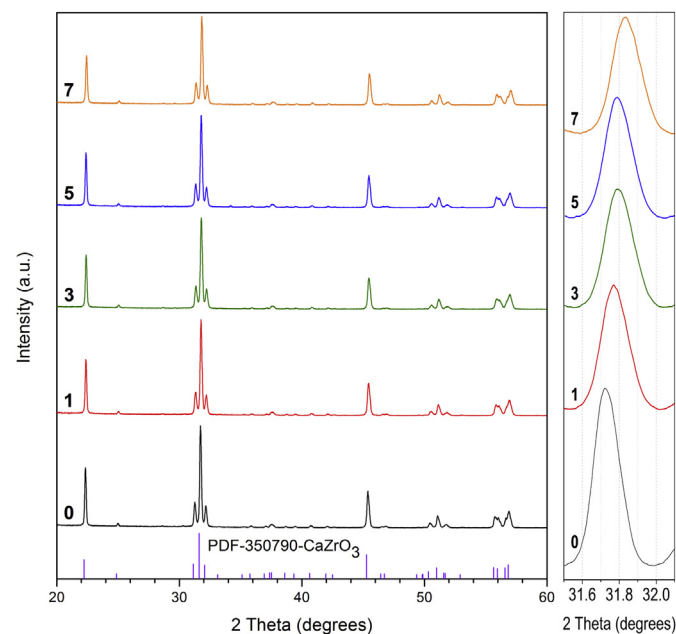


Fig. 2. XRD patterns of  $\text{CaZr}_{1-x}\text{Cr}_x\text{O}_3$  samples annealed at 1400 °C for 2 h.

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