Synthesis and characterization of Cr-doped diopside ceramics

Синтез и характеристика на хром-съдържаща керамика, базирана на диопсид

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Abstract. A series of ceramics in the system CaO–Cr₂O₃–MgO–SiO₂ was synthesized via solid-state high temperature sintering at 1000, 1100 and 1200 °C. The resulting ceramics were examined by powder X-ray diffraction, scanning electron microscopy, infrared and electron paramagnetic resonance spectroscopy. The color characteristics were measured spectrophotometrically. It was found that under the synthesis conditions multiphase ceramics were obtained which contain diopside, wollastonite, magnesiochromite, cristobalite, tridymite and periclase in various proportions. The synthesized ceramics are gray, gray-green and green in color, depending on the content of Cr additive, temperature of furnace and phase composition.

Keywords: ceramics, chromium, diopside, mineral composition, pigments, color indices.

Introduction

The pyroxene group minerals have the general formula M₂²⁺M₁²⁺T²⁺O₆, where M₂ refers to cations in a generally distorted octahedral coordination, M₁ to cations in a regular octahedral coordination, and T to tetrahedrally coordinated cations. The T-site is mainly occupied by Si and (Si⁴⁺, Al³⁺, Fe³⁺) in the case of silica undersaturated end members of the group. The M₁-site is occupied by Mg²⁺, Fe²⁺, Co²⁺, Al³⁺, Fe⁴⁺, Cr³⁺, V⁴⁺, Ti⁴⁺, Ti³⁺, etc., while the M₂-site mainly by Ca²⁺, Na⁺, Mg²⁺, Fe²⁺ (Morimoto et al., 1988). Single chains of SiO₄ tetrahedra extending parallel to c axis determine the pyroxene crystal structure. The chain structure offers much flexibility in the incorporation of various cations, which is limited by the size of the sites in the structure and the charge of the substituting ions. The choice of pyroxene matrix for the production of ceramic pigments is determined by the advantage that the synthesis of diopside can be carried out at temperatures below 1300 °C without use of mineralizers (Pogrebennkov et al., 1996).

A ceramic with an initial composition corresponding to stoichiometric diopside, solid-state sintered at 1200 °C was recently reported, and the quantitative phase composition was determined to be 66 wt% diopside, 19 wt% wollastonite, 10 wt% åckermanite, 4 wt% periclase and 1% cristobalite (Titorenkova et al., 2022). Doping with different transition metals will have an effect on the incorporation of chromophoric impurities into the ceramics in a different form, depending on the initial concentration of the reagents, the phase composition and the sintering temperature. Successful experiments have been carried out for the synthesis of pink-colored cobalt-diopside ceramics (Montovani et al., 2015; Titorenkova et al., 2022). Incorporation of trivalent chromophore impurities is more difficult because it leads to a change in phase composition and requires a more complex mechanism for isomorphous incorporation into the diopside structure.
When Mg$^{2+}$ is substituted by Cr$^{3+}$, coupled substitution is required to compensate the charge by scheme $2R^2+(R^3+) \leftrightarrow R^2+(R^3+)$. In ceramic syntheses, such charge compensation can be realized by adding NaF mineralizer to the system. Another mechanism for obtaining green colored ceramics is to modify the system by adding only chromium oxide to produce chromium spinel. It is known, that in the preparation of synthetic glass-ceramics, Cr$_2$O$_3$ is used as an effective nucleating agent inducing formation of a spinel phase and controlling the crystallization of diopside phase (Zhang et al., 2018; Eoh, Kim, 2014; Barbieri et al., 1994; Rezvani et al., 2005). Therefore, we assume that the addition of Cr$_2$O$_3$ will contribute to the crystallization of chromium spinel and diopside. The aim of the present study is to obtain colored, high-temperature, Cr containing ceramics with various initial concentration of chromium additives at three different temperatures of sintering, as well as to study the change in the phase composition and color.

Materials and method of synthesis

For the preparation of ceramics in the system CaO–Cr$_2$O$_3$–MgO–SiO$_2$, we introduce chromium by calculating its amounts, following the expression CaO. xCr$_2$O$_3$. (1–x)MgO.2SiO$_2$, where x = 0.1, 0.2, 0.3, 0.4 and 0.5. Chromium doped ceramics were synthesized via solid-state high temperature sintering method.

Starting materials used for the synthesis are analytical grade CaCO$_3$, Cr$_2$O$_3$, MgO (Merck) and amorphous silica (SiO$_2$.nH$_2$O). Calculated quantities of materials for 100 g batch are weighed, then mixed and dry homogenized in planetary mill Pulverizete-6 (Fritsch). Synthesis was carried out in a laboratory muffle furnace in porcelain crucibles with a heating rate of 300–400 °C/h in air with isothermal retention of 2 hours at the final temperature. The resulting powder mixtures were sintered at 1000, 1100 and 1200 °C in order to obtain colored Cr-doped ceramics.

The phase composition of the synthesized ceramic pigments was determined using X-ray Diffractometer Empyrean, Malvern Panalytical, operating at 40 kV and 30 mA with CuKα radiation.

Fourier transform infrared (FT-IR) spectra were collected using Tensor 37 spectrometer (Bruker) with 4 cm$^{-1}$ resolution after averaging 128 scans on standard KBr pallets in the spectral region 400–4000 cm$^{-1}$ at room temperature.

EMXplus Spectrometer System (Bruker) was used to perform electron paramagnetic resonance (EPR) spectroscopy in the 9.4 GHz X-band region.

The color of the pigments is determined by Lovibond Tintometer RT 100 Color.

Result and discussion

The synthesized ceramics based on stoichiometric diopside in the system CaO–MgO–2SiO$_2$ are white-colored with polyphase composition. The main phase is diopside, together with different amounts of wollastonite, åkermanite and SiO$_2$, depending on the sintering temperature (Titorenkova et al., 2022). The addition of chromium to the system leads to change in the phase composition and formation of green-colored chromium spinel together with diopside.

<table>
<thead>
<tr>
<th>Initial composition</th>
<th>T, °C</th>
<th>Mineral phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO.0.1Cr$_2$O$_3$.0.9MgO.2SiO$_2$</td>
<td>1000</td>
<td>Di, Mer, Wo, Per</td>
</tr>
<tr>
<td>CaO.0.1Cr$_2$O$_3$.0.9MgO.2SiO$_2$</td>
<td>1100</td>
<td>Di, Mer, Wo, Per</td>
</tr>
<tr>
<td>CaO.0.1Cr$_2$O$_3$.0.9MgO.2SiO$_2$</td>
<td>1200</td>
<td>Di, Mer, Crs, Wo, Trd</td>
</tr>
<tr>
<td>CaO.0.2Cr$_2$O$_3$.0.8MgO.2SiO$_2$</td>
<td>1000</td>
<td>Di, Mer, Wo, Per</td>
</tr>
<tr>
<td>CaO.0.2Cr$_2$O$_3$.0.8MgO.2SiO$_2$</td>
<td>1100</td>
<td>Di, Mer, Wo, Per</td>
</tr>
<tr>
<td>CaO.0.2Cr$_2$O$_3$.0.8MgO.2SiO$_2$</td>
<td>1200</td>
<td>Di, Mer, Crs, Wo, Trd</td>
</tr>
<tr>
<td>CaO.0.3Cr$_2$O$_3$.0.7MgO.2SiO$_2$</td>
<td>1000</td>
<td>Di, Mer, Wo, Cr$_2$O$_3$</td>
</tr>
<tr>
<td>CaO.0.3Cr$_2$O$_3$.0.7MgO.2SiO$_2$</td>
<td>1100</td>
<td>Di, Mer, Wo, Crs, Cr$_2$O$_3$</td>
</tr>
<tr>
<td>CaO.0.3Cr$_2$O$_3$.0.7MgO.2SiO$_2$</td>
<td>1200</td>
<td>Di, Mer, Wo, Crs, Cr$_2$O$_3$</td>
</tr>
<tr>
<td>CaO.0.4Cr$_2$O$_3$.0.6MgO.2SiO$_2$</td>
<td>1000</td>
<td>Di, Mer, Wo, Cr$_2$O$_3$</td>
</tr>
<tr>
<td>CaO.0.4Cr$_2$O$_3$.0.6MgO.2SiO$_2$</td>
<td>1100</td>
<td>Di, Mer, Wo, Cr$_2$O$_3$</td>
</tr>
<tr>
<td>CaO.0.4Cr$_2$O$_3$.0.6MgO.2SiO$_2$</td>
<td>1200</td>
<td>Di, Mer, Wo, Crs, Cr$_2$O$_3$</td>
</tr>
<tr>
<td>CaO.0.5Cr$_2$O$_3$.0.5MgO.2SiO$_2$</td>
<td>1000</td>
<td>Di, Mer, Wo, Cr$_2$O$_3$</td>
</tr>
<tr>
<td>CaO.0.5Cr$_2$O$_3$.0.5MgO.2SiO$_2$</td>
<td>1100</td>
<td>Di, Mer, Wo, Crs, Cr$_2$O$_3$</td>
</tr>
<tr>
<td>CaO.0.5Cr$_2$O$_3$.0.5MgO.2SiO$_2$</td>
<td>1200</td>
<td>Di, Mer, Wo, Crs, Cr$_2$O$_3$</td>
</tr>
</tbody>
</table>

Abb.: Di, diopside; Mer, magnesiochromite; Wo, wollastonite; Per, periclase; Crx, cristobalite; Trd, tridymite; Cr$_2$O$_3$, chromium oxide.
**X-ray diffraction (XRD) analysis**

The powder XRD data revealed that the ceramics synthesized at different temperature and initial concentration of chromium additive, vary in their phase composition (Table 1). The main crystal phases are diopside (CaMgSi$_2$O$_6$), magnesiochromite (MgCr$_2$O$_4$) – chromium spinel, wollastonite (CaSiO$_3$), periclase (MgO), cristobalite (SiO$_2$), tridymite (SiO$_2$), and eskolaite (Cr$_2$O$_3$).

X-ray diffraction patterns of the synthesized ceramics are shown on Fig. 1a–c.

At 1000 °C polyphase ceramic that contains diopside (D), magnesiochromite (M), and wollastonite (W) is obtained. At low initial concentration of chromium (x = 0.1 and 0.2) diopside, wollastonite and magnesiochromite are prevailing phases. Unreacted magnesium forms periclase. At higher concentration of Cr in the initial batch (x ≥ 0.3), unreacted Cr$_2$O$_3$ remains.

The samples heated at 1100 °C reveal the presence of diopside (D), magnesiochromite (M), and wollastonite (W) with some unreacted MgO at concentrations of Cr$_2$O$_3$ x = 0.1 and 0.2. With the addition of Cr$_2$O$_3$ ≥ 0.3 unreacted Cr$_2$O$_3$ and SiO$_2$ (as cristobalite) are observed.

The XRD patterns of the samples heated at 1200 °C exhibit lines of diopside (D), magnesiochromite (M), and wollastonite (W). Cristobalite and tridymite are concomitant phases. At concentrations of Cr$_2$O$_3$ x = 0.1, 0.2, and 0.3 the predominant phase is diopside. At higher concentrations of chromium additive (x ≥ 0.3) unreacted Cr$_2$O$_3$ remains.

**FTIR spectra**

FT-IR spectra of Cr-doped ceramics sintered at 1000, 1100 and 1200 °C reveal strong peaks near 1076 and 967 cm$^{-1}$ which are due to Si-O stretching vibration in diopside. Peak at 515 cm$^{-1}$

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**Fig. 1.** XRD patterns of samples with different chromium loading in the initial batch after sintering at 1000 °C (a), 1100 °C (b) and 1200 °C (c); IR spectra of samples with different chromium loading in the initial batch after sintering at 1200 °C (d). Abb.: D, diopside; M, magnesiochromite; W, wollastonite; P, periclase, C, cristobalite; T, tridymite; *, chromium oxide.
is characteristic for O-Mg-O bending vibrations in diopside (Omori, 1971). The peaks of diopside overlap with those of wollastonite, which should be at 1060, 1000 and 900 cm\(^{-1}\) (Chukanov, 2014). Also, SiO\(_2\) polymorphs tridymite and cristobalite have strong infrared absorption in the range 1080–1200 and at 480 cm\(^{-1}\). Infrared absorption spectrum of magnesiochromite should have strong absorption band near 625 cm\(^{-1}\) according Chukanov (2014). In the same spectral range, the band of Cr\(_2\)O\(_3\) overlap.

Electron paramagnetic resonance (EPR)

EPR analysis were measured at temperatures of 100, 295 and 370 K of samples with initial chromium loading \(x = 0.1, 0.3\) and 0.5 sintered at 1200 °C. The value of the g-factors and the temperature dependence of the width of the narrow signal in the EPR spectra allow us to attribute it to antiferromagnetically bounded Cr\(^{3+}\) ions (S=3/2) (Vijay et al., 2009). Based on these parameters, the signal can be related to Cr\(^{3+}\) ions, most likely located in anti-ferromagnetic phase magnesiochromite with spinel type of crystal structure – MgCr\(_2\)O\(_4\). The obtained result is in a good agreement with the XRD analysis data. In addition, the amount of this phase depends nonlinearly on the total amount of Cr\(^{3+}\) loading. The broad signal observed at temperatures above 350 K, in sample with \(x = 0.5\) can be attributed to Cr\(^{3+}\) in Cr\(_2\)O\(_3\) (Kittel, 2005).

Color measurement

The color of the resulting ceramics was defined according to universal CIELab system. In the CIELab space, the color is defined by three coordinates. The lightness value, \(L^*\), ranges from absolute white \(L^* = 100\) to absolute black \(L^* = 0\). The \(a^*\) axis represents the green–red opponent colors, with negative values toward green and positive values toward red. The \(b^*\) axis indicates the blue–yellow opponents, with negative numbers toward blue and positive toward yellow. The color measurements for ceramics sintered at 1100 °C reveal that the \(L^*\) value decreases with increasing initial Cr content from 75.5 (\(x = 0.1\)) to 59.6 (\(x = 0.5\)). The value of green color (\(a^*\)) increases with increase of initial chromium content from –2.7 to –10.7, respectively. And the value of yellow color (\(b^*\)) only slightly increases.

Conclusions

The addition of chromium oxide in the initial diopside based system leads to the formation of polyphase ceramics. Depending on the initial Cr additive, temperature of furnace and phase composition, the resulting ceramics are gray, gray-green and green in color. At initial chromium loading \(x = 0.1\) and 0.2 the predominant phases are diopside and chromium spinel – magnesiochromite, which colors the ceramics in green. Higher levels of chromium loading interfere due to the presence of eskolaite.

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References


