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SYNTHESIS AND CHARACTERIZATION OF V - DOPED DIOPSIDE CERAMIC PIGMENTS

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Abstract: *Ceramics are synthesized via solid-state high temperature sintering at a temperature of 1000, 1100 and 1200°C in the system $CaO.xV_2O_5.(1-x)MgO.2SiO_2$, where x = 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6. The obtained ceramics were examined by powder X-ray diffraction analysis, electron scanning microscopy, infrared and UV-Vis spectroscopy. It has been found that under synthesis conditions a multiphase ceramics is obtained which contains in different ratio diopside, cristobalite, tridymite and traces of wollastonite. The colour of the ceramic changes to blue-greenish when vanadium is added to the system. The high concentration of vanadium leads to the formation of various polymorphic phases of SiO_2 and inhibits the formation of diopside. The efect of vanadium concentration and sintering temperature on phase composition and colour was studied.*

Keywords: *pigments, colour, ceramic, diopside*

INTRODUCTION

Ceramic pigments are inorganic materials containing chromophore elements that are added to produce the corresponding colour. Diopside ($MgCaSi_2O_6$) is Ca-rich pyroxene which is characterized by octahedral coordinated Mg^{2+} ions and tetrahedral coordinated Si^{4+} ions, with Ca^{2+} in 8- fold coordination crystallized in space group C2/c. The content of calcium oxide CaO is 25.9%, magnesium oxide MgO -18.5% and silicon oxide SiO_2 - 55.6% (Cameron M. & al., 1973). Ceramic pigments can be expected in the $CaO-MgO-SiO_2$- (RO or R_2O_3) system, where RO is CoO, NiO, MnO; R_2O_3 - Fe_2O_3, Cr_2O_3, V_2O_3, where magnesium and calcium can be partially replaced by chromophore elements (Pishch I., 1981), (Sedelnikova M. and V. Pogrebenkov, 2006), (Pogrebenkov V., M. Sedelnikova and V. Vereshchagin, 1999). The choice of diopside matrix for the proposed ceramic pigments is determined by the crystal-chemical characteristics of the minerals of the pyroxene group, which form solid solutions with complete or limited isomorphic substitution and also by the advantage that synthesis of diopside can be carried out at relatively low temperatures without using mineralizers (Mantovani L. & al., 2015), (Lakov L. & al., 2020), (Belyi Y., A. Zaichuk, 2005).

The aim of this study is to obtain vanadium-doped diopside based ceramic pigments with various concentrations of V and to determine the phase composition at different temperatures of sintering and vanadium concentration. To achieve these goals, ceramics are synthesized via solid-state high temperature sintering at 1000, 1100 and 1200°C in the system $CaO.xV_2O_5.(1-x)MgO.2SiO_2$, where x = 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6.

Materials and method of synthesis

Starting materials used for the synthesis are $CaCO_3$, NH_4VO_3, MgO and $SiO_2.nH_2O$ with particle size in the range of 2-7μm, which is much more reactive than conventionally used quartz sand as a source of SiO_2. Calculated quantities of materials for 100 g batch are weighed with a

precision, then mixed and dry homogenized in planetary mill Pulverizete-6 (Fritch). 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 hour at the final temperature. The resulting powder mixtures were sintered at 1000, 1100 and 1200°C in order to obtain V-doped diopside.

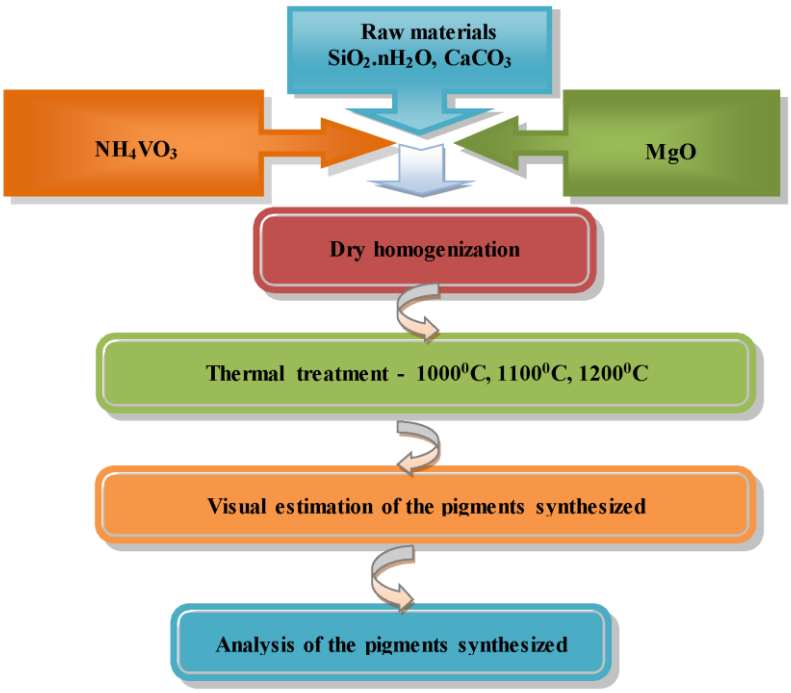

Fig. 1. The technological scheme for the synthesis of pigments

The resulting ceramic were examined by powder X-ray diffraction (XRD) analysis, electron microscopy, infrared spectroscopy and the color was determined spectrophotometrically.

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

FT- IR spectra were collected using a 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.

Electron probe microanalyses (EPMA) and secondary electron (SE) images of the materials were carried out on ZEISS SEM EVO 25 LS –EDAX Trident (IMC-BAS) at acceleration voltage of 20 kV and beam current of 500 pA.

The colour of the pigments is determined by tintometer (Lovibont Tintometer RT 100 Colour) and presented in the CIELab colour space as defined by the International Commission on Illumination (CIE).

RESULTS AND DISCUSSION

Powder XRD patterns of synthesized ceramic pigments in the system CaO. xV_2O_5.(1-x)MgO. $2SiO_2$, at different temperatures (1000°C; 1100°C; 1200°C) and initial vanadium content x = 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6. The powder XRD data revealed that the ceramics synthesized at different temperature and vanadium concentration vary in their phase composition.

The XRD patterns, presented on Figure 2 show well defined peaks corresponding to Diopside - $CaMg(Si_2O_6)$; Wollastonite - $CaSiO_3$; Cristobalite - SiO_2; Tridymite - SiO_2 determined using the Powder Diffraction File (PDF) of the International Centre for Diffraction Data - ICDD.

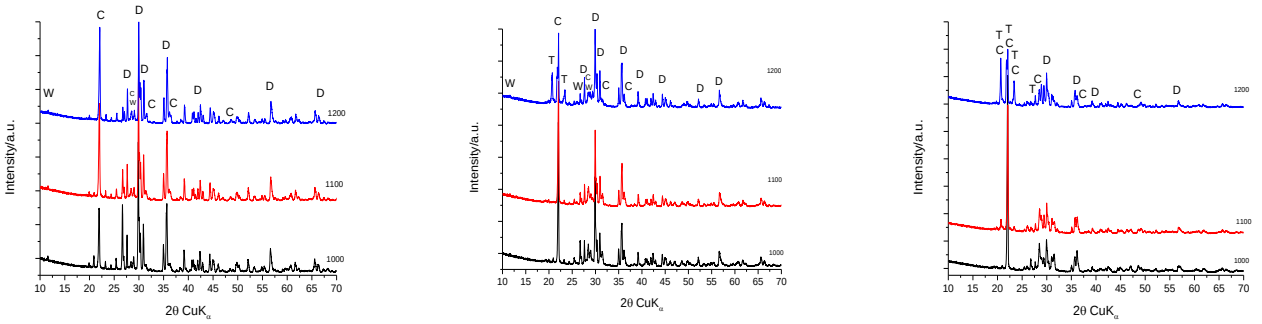

Figure 2. Powder XRD paterns of samples with 0.1; 0.3 and 0.6 V_2O_5 sintered at 1000, 1100 and 1200 ^oC: D - Diopside, W - Wollastonite, C - Cristobalite, T – Tridymite

At low concentrations of V_2O_5 /0.1 - 0.3/ the main diopside phase is synthesized even at 1000^{o}C. No separate vanadium phases are formed, which means that vanadium was successfully doped in the diopside structure. Wollastonite and cristobalite are also formed. With increasing temperature of synthesis up to 1100^{o}C wollastonite phase almost disappeared. An increase in temperature to 1200^{o}C leads to increase of cristobalite and appearance of trydimite. At higher concentrations of V_2O_5 /0.4 - 0.6/ the formation of diopside is suppressed at the expense of SiO_2 phases. The optimal composition is $CaO.0,3V_2O_5.0,7MgO.2SiO_2$ and temperature for synthesis at 1100°C.

FT-IR spectra of the vanadium doped ceramic are presented on Figure 3. Strong peaks at 1072 and near 975 – 965 cm^{-1} are due to Si-O stretching in dioside. Peak at 515 cm^{-1} is characteristic for O-Mg-O bending vibrations in diopside (Omori K., 1971). As the vanadium concentration increases, the most intensive diopside peak, centered at 1072 cm^{-1}, shifts to higher wavenumbers. Another peak also appears near 1200 cm^{-1}. This confirms the increase of SiO_2 phases with vanadium concentration. Peak around 625 cm^{-1} may be associated with the appearance of cristobalite.

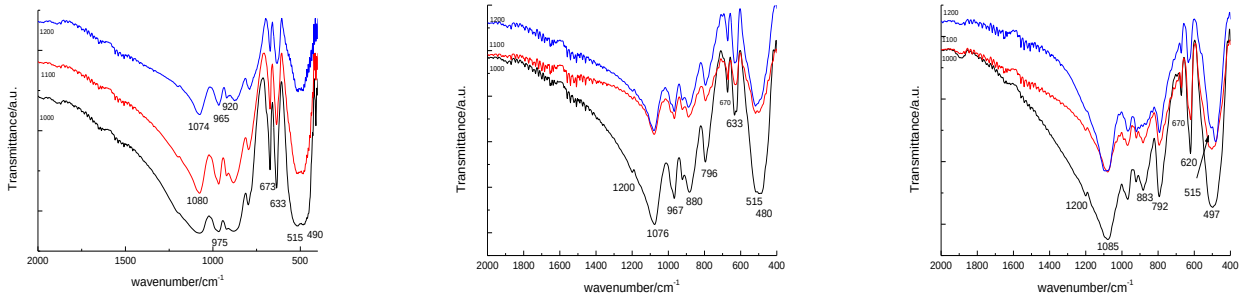

Figure 3. FT-IR spectra of samples with 0.1, 0.3 and 0.5 V_2O_5 sintered at 1000, 1100 and 1200^{o}C

The very strong and broad FTIR band at 1085-1200 cm^{-1} is usually assigned to Si – O – Si asymmetric stretching vibrations. The band at 798 cm^{-1} can be assigned to Si – O – Si symmetric stretching vibrations, whereas the FTIR band at 460 cm^{-1} is due to O – Si – O bending vibrations in SiO_2.

Colour is one of the most important indicators of the quality of pigments. Coloured substances absorb light of a certain wavelength in the visible range of spectrum. The colour change is evidence that the chromophore element is present in the diopside. The CIELab system is universal and determines the colours not only of ceramic pigments, but also of other materials and has a wide application. In the CIELab system the colour coordinates are respectively:

- L * - brightness, L * = 0 - black colour, L * = 100 - white colour
- a * - green (-) / red (+); - b * - blue colour (-) / yellow colour (+)

The colour space of the CIELab system is shown in Figure 4. The results obtained for colour coordinates of the pigments are shown in Table 1.

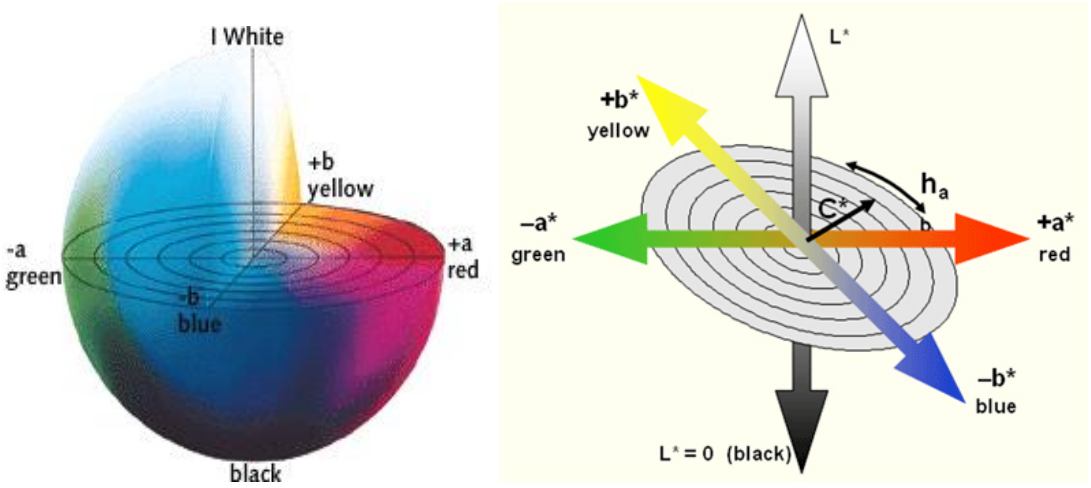

Figure 4. The colour space of CIELab system

Table 1. Results obtained for colour coordinates of the pigments

№	Composition	Colour	L*	a *	b *
1	CaO.0,1V_2O_5.0,9MgO.2SiO_2 - 1000°C		83,8	-9,3	-6,4
2	CaO.0,1V_2O_5.0,9MgO.2SiO_2 - 1100°C		87,2	-10,2	-2,8
3	CaO.0,1V_2O_5.0,9MgO.2SiO_2 - 1200°C		86,2	-11,2	1,0
4	CaO.0,2V_2O_5.0,8MgO.2SiO_2 - 1000°C		79,9	-11,9	-3,2
5	CaO.0,2V_2O_5.0,8MgO.2SiO_2 - 1100°C		84,4	-13,2	2,2
6	CaO.0,2V_2O_5.0,8MgO.2SiO_2 - 1200°C		93,4	-3,9	6,1
7	CaO.0,3V_2O_5.0,7MgO.2SiO_2 - 1000°C		78,2	-12,7	-1,9
8	CaO.0,3V_2O_5.0,7MgO.2SiO_2 - 1100°C		84,3	-14,5	3,9
9	CaO.0,3V_2O_5.0,7MgO.2SiO_2 - 1200°C		92.4	-3,9	5,7
10	CaO.0,4V_2O_5.0,6MgO.2SiO_2 - 1000°C		77,7	-12,4	0,1
11	CaO.0,4V_2O_5.0,6MgO.2SiO_2 - 1100°C		84,1	-12,4	5,0
12	CaO.0,4V_2O_5.0,6MgO.2SiO_2 - 1200°C		90,6	-3,6	7,6

From the presented data it can be seen that the colour of the synthesized pigments is light blue-green. The color change is evidence that the chromophore element is present in the diopside. With increase of temperature of sintering up to 1200°C, an increase in brightness L* is observed. The amount of blue colour (-b*) is greatest (b*=-6.4) in the pigments sintered at 1000°C with

composition $CaO.0,1V_2O_5.0,9MgO.2SiO_2$. The green colour is greatest (a*=-14.5) in the pigment with composition $CaO.0,3V_2O_5.0,7MgO.2SiO_2$ synthesized at 1100°C.

At 1200°C for all samples, the colour disappears and the powders become almost white. This is in agreement with XRD and IR data.

To determine the topography of the samples studied, scanning electron microscopy (SEM) was employed. The particles are opaque for the electron beam and conclusions only on the shape and size of the crystals could be made, as well as their affinity to aggregation. Scanning electron images of sintered at 1000, 1100 and 1200°C (Figure 5) samples with different nickel content reveal that powder sample is composed of dense aggregates.

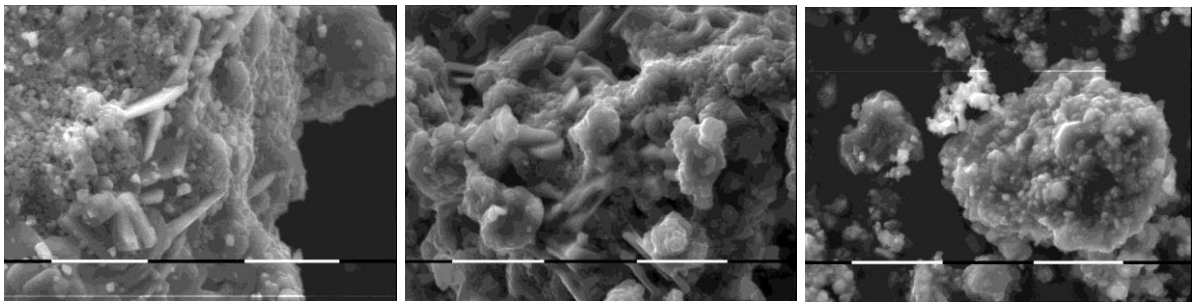

Figure 5. SEM images of $CaO.0,3V_2O_5.0,7MgO.2SiO_2$ at 1000, 1100 and 1200°C ; Marker = 10μm

The SEM images show the formation of crystals even at 1000°C, and at 1200°C temperatures dence sintering is observed.

CONCLUSIONS

Vanadium doped blue-green ceramic pigments based on diopside were synthesized by the method of solid-phase sintering. The phase composition was determined. The optimal parameters of the synthesis process have been established. The best results were obtained with the pigment with a concentration of $0.3V_2O_5$ at 1100°C. The high concentration of vanadium leads to the formation of various polymorphic phases of SiO_2 and inhibits the formation of diopside. The synthesized pigments are promising to be applied in glazes for tiles and sanitary ceramics.

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