SYNTHESIS AND STUDY OF GARNET CERAMIC PIGMENTS IN THE SYSTEM $CaO.Cr_2O_3.SiO_2$

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Abstract

The aim of paper the synthesis of new garnet ceramic pigments. The blend preparedwas ground in a ball mill and subjected to heat treatment. Green ceramic pigments were synthesized at 800°C - 1200°C. The optimal temperature for the synthesis and the most appropriate mineralizer were defined. The phases established by X-ray diffraction and infrared spectroscopy are the following minerals: $Ca_3Cr_2Si_3O_{12}$ - uvarovite, $CaSiO_3$ – wollastonite, SiO_2 – cristobalite.

The colour characteristics were measured spectrophotometrically with Tintometr RT 100 Lovibond. The particle sizes of the pigments were determined by transmission electron microscopy. The best pigments are applied in white cover glaze for faience.

Key words: *pigments, colour, ceramic, garnet*

INTRODUCTION

Ceramic pigments are inorganic colored finely dispersed powders which, when added to a material, impart certain color and change some of its properties. The pigments impart color due to the selective absorption of light waves with certain wavelengths by its crystal lattice. As a result, the pigments are colored in a color complement to the absorbed one. Most often, the color carriers of the pigments are chromophores. The latter are atoms and atom aggregations which possess the ability to impart one or another color to the substances which they are added to [1].

One of the most perfect classifications is that of Tumanov which is based on the crystalline structure of the main phase. According to this classification, pigments are spinel, garnet, zircon, villemite, mullite and other types. Furthermore, the use of this property for the classification provided wide possibilities for purposeful synthesis of pigments of various colors.

Garnets are a group of minerals different by composition but with analogous chemical formulae and similar appearance of their crystals. The transparent saturated colored garnets are demanded precious stones. The name of the group comes from the Latin word granatus which stands for the seeds of the granate tree. Garnets have various colors: purple red – almandine, colorless of yellow-green – grossular, brown or black – melanite, green – uvarovite, red – pyrope and andrdite, etc.

Recently, researchers of many countries work on the synthesis, characterization and properties of various kinds of garnet ceramic pigments obtained both from traditional raw materials and waste products.[1-5]

Among the known garnet chromium containing minerals, uvarovite ($3CaO{\cdot}Cr_2O_3{\cdot}3SiO_2$) is colored in green and is resistant to temperatures up to 1370^0C. On its basis, ceramic pigments are prepared are widely used for the preparation of glaze and enamel green coatings, as well as various kinds of green colored ceramic pigments.

The aim of the present work is to synthesize, study and characterize garnet ceramic pigments belonging to the system $CaO.Cr_2O_3.SiO_2$**.**

ИЗЛОЖЕНИЕ

Materials and method of synthesis

For the preparation of garnet ceramic pigments in the system $CaO.Cr_2O_3.SiO_2$, the blends were defined on the basis of the stoichiometry of the main mineral – uvarovite $Ca_3Cr_2(SiO_4)_3$. The following composition was selected for the pigments – $3CaO.Cr_2O_3.3SiO_2$. The mineralizer used in the synthesis to decrease the synthesis temperature and accelerate the processes of formation of the

new phase was H_3BO_3. The materials used for the synthesis were CaO, Cr_2O_3, $SiO_2.nH_2O$ and H_3BO_3.

The substance used to introduce SiO_2 into the system – $SiO_2.nH_2O$, is much more reactive than the common quartz sand and the particle sizes were dispersed in the range 2-7μm. Initially, after the heating in a platinum crucible, the contents of SiO_2 and H_2O in $SiO_2.nH_2O$ was determined to be: SiO_2 - 76,3% and H_2O - 23,7%.

The quantities of the materials from which 100 g blend is prepared were weighed with precision of 0,1 g, then they were mixed and homogenized in dry state in a planetary mill PULVERIZETE – 6, product of"FRITCH".

The sintering was carried out in a laboratory muffle oven at heating rate – 300-400^oC/h in air atmosphere; the blend was placed in a porcelain crucible with a lid. The isothermal period at the final temperature was 2 hours. The pigments were sintered at 800^oC, 900^oC, 1000^oC, 1100^oC and 1200^oC. The technological scheme of the synthesis of the pigments is presented in Fig. 1.

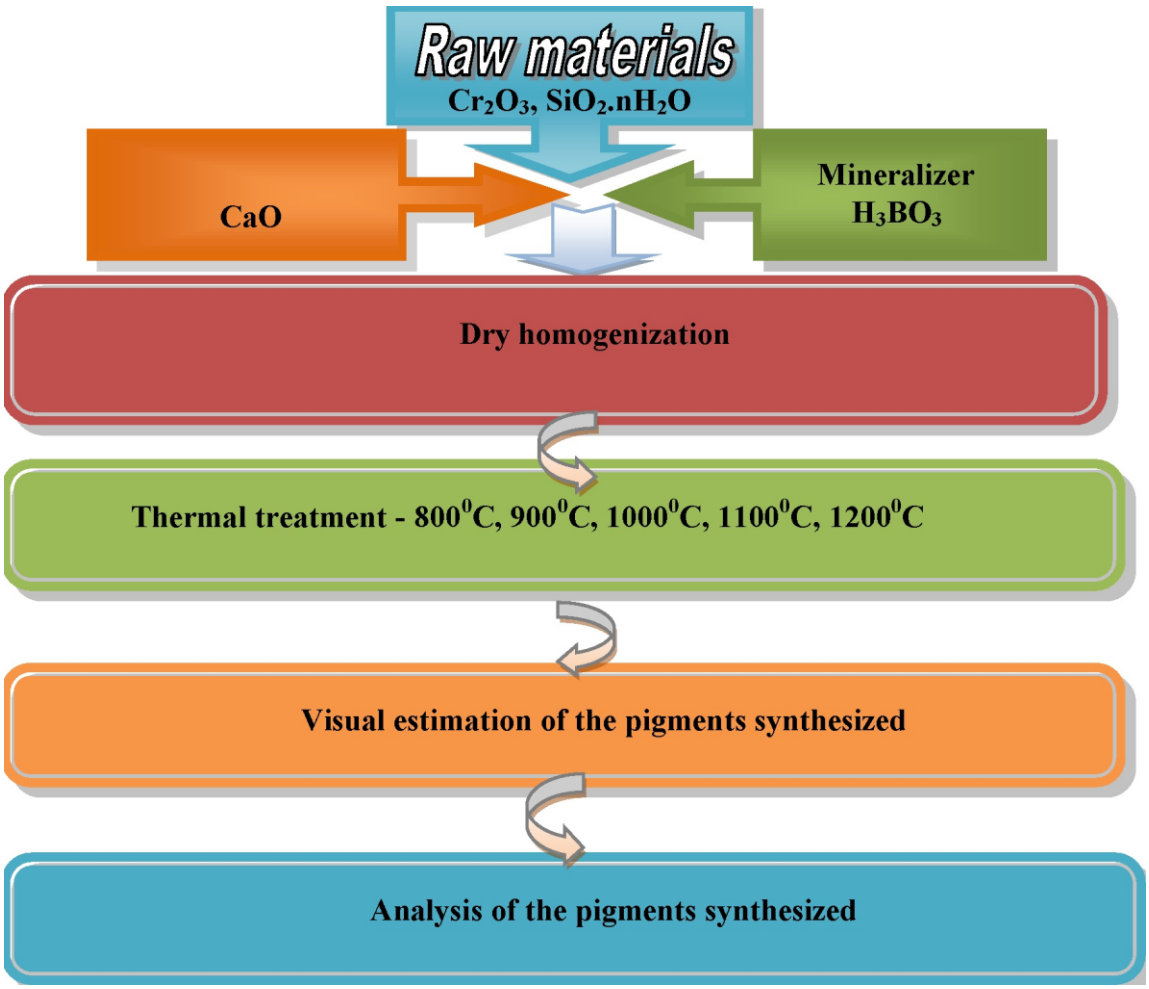

Fig.1. Technological scheme for synthesis of pigments

STUDIES OF THE PIGMENTS OBTAINED

X-ray phase analysis of the ceramic pigments obtained

X-ray phase analysis as a direct method for identification of phases. It is based on the diffraction of X-rays. The main task of the X-ray analysis was to identify the different phases individually or aim blends using the diffraction pattern registered from the sample studied.

The basic method of the phase analysis is the powder method which is widely used due to its

simplicity and ease of versatility. The X-ray studies were performed on an apparatus IRIS with Cu K_α radiation and nickel filter, in the range of angles from 2 to 80°. The interplanar distances (d, nm) were calculated by the formula of Wulf-Bragg: $n.\lambda = 2d.\sin\theta$, where: λ – X-ray wavelength, nm; n – diffraction order (n = positive integer); θ – Bragg's angle of diffraction, grad.

X-ray patterns of the garnet ceramic pigments synthesized are presented in Fig.2.

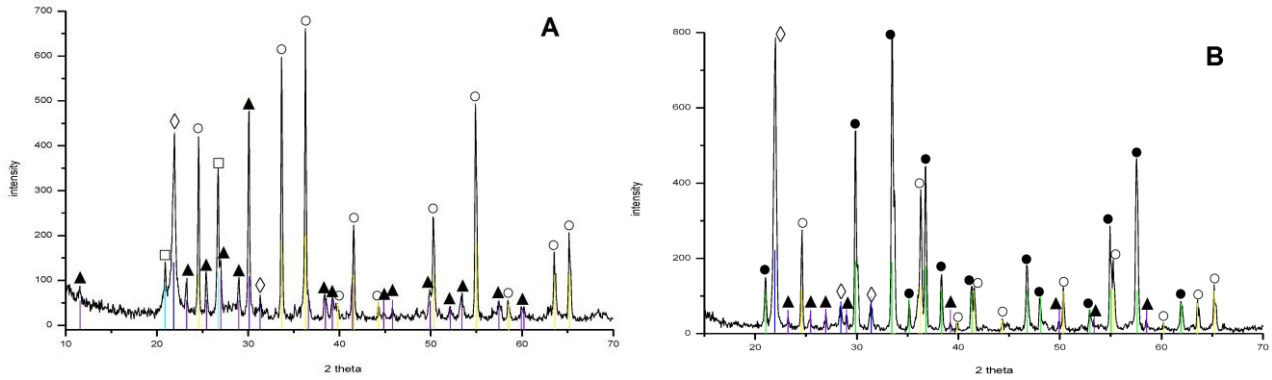

Fig.2 X-ray patterns of pigments in the system $3CaO.Cr_2O_3.3SiO_2$ taken at 900°C (A), 1100°C (B)

● - Uvarovite $Ca_3Cr_2Si_3O_{12}$ - 87 - 1007 ▲ - Wollastonite $CaSiO_3$ - 84 - 0654
◊ - Crystobalite SiO_2 - 89 - 3434 □ - Quartz SiO_2 - 79 – 1910
○ - Chromium oxide Cr_2O_3 - 82 - 1484

The pigments synthesized had stable green color and significant formation of the main phase – the mineral uvarovite $Ca_3Cr_2(SiO_4)_3$, was observed at 1100°C, although reflexes from wollastonite ($CaSiO_3$), crystobalite (SiO_2) Cr_2O_3 were also observed. Supposedly, the full transformation will occur at 1200°C and isothermal period of 2 h.

Color measurements

Color is one of the most important properties of the pigments. Colored substances absorb and transform light of certain wavelengths within the visible spectrum due to their atomic structure. Using the CIELab, not only the colors of ceramic pigments are determined but also these of other materials which means that this system is universal and it is widely used.

In the system CIELab, the color co-ordinates determined are as follows:

- L* - lightness, L*=0 – black color, L*=100 – white color
- a* - green color (-) / red color (+)
- b* - blue color (-) / yellow color (+)

The color space of the system CIELab is shown in Fig.3.

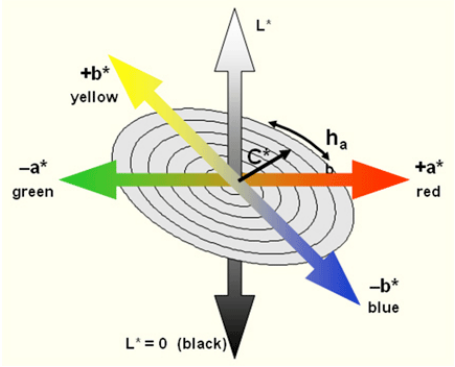

Fig.3 Color space of CIELab

The colors of the pigments were determined spectrometrically with a Tintometer RT 100 Colour. The results obtained from the measurements are presented in Table 1.

Table 1 Results obtained from the measurement of the color co-ordinates

Pigment	Color	R	G	B	L*	a*	b*
$3CaO.Cr_2O_3.3SiO_2$ 900°C		143,4	149.2	128.4	59,6	-10,2	9,2
$3CaO.Cr_2O_3.3SiO_2$ 1000°C		123,4	141.9	119,1	57,1	-10,9	9,9
$3CaO.Cr_2O_3.3SiO_2$ 1100°C		116,8	134,8	101,1	54,3	-13,4	15,9
$3CaO.Cr_2O_3.3SiO_2$ 1200°C		116,2	142,4	97,3	56,0	-18,1	21,5

It can be seen from the data presented that the co-ordinates R, G, B and L* decreased with the increase of the sintering temperature. The highest amount of green color /- a*/ was found for the pigment synthesized at 1200°C.

Electron microscopic studies of the pigments

Electron microscopy is a method for direct observation of the structure of the samples studied. To determine the topography of the samples studied, scanning electron microscopy (SEM) was employed. The SEM observations were carried out on an apparatus TESCAN, SEM/FIB LYRA I XMU at 30 kV accelerating voltage. The observations were accompanied by energy-dispersive X-ray spectroscopy (EDS) carried out with detector of Bruker.

The pigments synthesized were observed in regime of reflected electrons at low **(**1500x) and high – (3000x) magnification. The electron microscopic observations were combined with mapping EDS to view the distribution of the elements among the crystalline phases.

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. Fig.3 shows micrographs of the pigments synthesized.

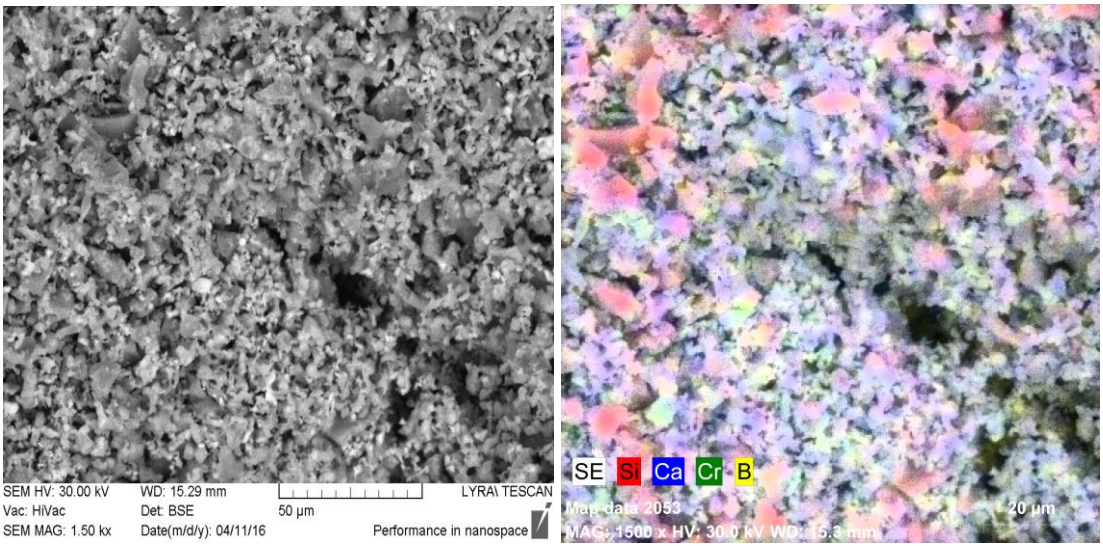

Fig. 3 Micrographs of the garnet ceramic pigments synthesized

As can be seen from the figure, the sample was polydispersed and contained two kinds of

crystals: one with particle size 1- 2 μm and the other between 6 – 8 μm. The presence of smaller crystals was due to exogenic polymineral processes of formation and they correspond to the solid solution between Cr_2O_3-SiO_2 with predominating content of SiO_2. The color transition from green to orange and red in the micrograph was due to the growth of the phase with the larger particles and recrystallization with formation of a new solid solution with final equilibrium composition $3CaO.Cr_2O_3.3SiO_2$ and stoichiometric ratio.

CONCLUSIONS

Green ceramic pigments were synthesized on the basis of the garnet uvarovite by the method of solid phase sintering. The optimal parameters of the process of synthesis were determined. The best results were obtained with the pigment synthesized at sintering temperature of 1100^oC. The pigments obtained are suitable and can successfully be use in glazes for tiles and sanitary ceramics.

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REFERENCES

[1] R. Eppler R., Selecting ceramic pigments, J. Am. Ceram. Soc. Bull., 1987, 66, 1600–1610

[2] Galindo, R., Llusar, M., Tena, M. A., Monrós, G., & Badenes, J. A., New pink ceramic pigment based on chromium (IV)-doped lutetium gallium garnet 2007, Journal of the European Ceramic Society, 27, 1, 199-205

[3] Alarcon, J., P. Escribamo, J. Gargallo, Cr-CaO-SiO_2 Bassed Ceramic Pigments, Br. Ceram. Trans. J.,1984, 83, 3, 81-83

[4] Carda, J., G. Monros, P. Escribano and J. Alarcon, J., Synthesis of uvarovite Garnet, 1989, Journal of the American Ceramic Society, 72, 160

[5] Klemme, S., J. van Miltenburg, P. Javorsky, F. Wastin,Thermodynamic properties of uvarovite garnet ($Ca_3Cr_2Si_3O_{12}$), 2005, American Mineralogist 90, 663–666