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SYNTHESIS OF GARNET PIGMENTS AT LOW TEMPERATURE

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Abstract: *Garnet ceramic pigments were synthesized by the method of solid-phase sintering. The starting materials are pure oxides: CaO, SiO2.nH2O. The following elements have been added as chromophores: V, Fe dnd Cr. For this purpose, the following raw materials were used: NH4VO3, Fe2O3 and K2Gr2O7. The pigments were synthesized at a final firing temperature of 1000 ° C. The color characteristics of the synthesized ceramic pigments were determined using a color measurement system - CIELab.*

Keywords: *garnet pigments, solid-state sintering, CIELab color measurement*

INTRODUCTION

The term pigments is used for black, white or colored inorganic powders which are insoluble in the substrate where they are introduced and remain unchanged neither physically or chemically therefrom. The pigments used for the production of common colored glazed and non-glazed tiles should show good thermal and chemical stability at high temperatures (1200-1250 ºC). The first stage of pigment production is the choice of raw materials which are mainly metal oxides or salts of the necessary metals with industrial chemical purity. (Alarcon, J. & al., 1984).

The inorganic pigments are applied in wide variety of products as dyes, ceramics and enamels because they possess high thermal and ultraviolet stability (Wendusu & al., 2013).

The aim of the present work is to synthesize garnet ceramic pigments from pure raw materials and study the possibilities for their application in the silicate industry.

EXPERIMENT

Methods

Color Measurement. The color determination of the pigments is determined spectrally by a tintometer of Lovibond Tintometer RT 100 Color.

Infrared spectroscopy.

The FT-IR - studies were performed on a Tensor 27 Fourier infrared spectrophotometer FT-IR (Bruker, Germany) in the interval 400 – 4000 cm^{-1} at resolution of 1 cm^{-1}. Measurements were carried out at room temperature. The sample (0,3 mg) was tableted with KBr (100 mg) at a pressure of 2-4 atm.

Materials

Garnet ceramic pigments were synthesized by the method of solid state sintering of pure oxides: CaO, $SiO_2.nH_2O$; the dyers added were: V, Fe, Cr, introduced with the following oxides: NH_4VO_3, Fe_2O_3 and $K_2Cr_2O_7$.

The blends' compositions are presented in Table 1.

Table 1. Initial materials

№ of the sample	Composition	Synthesis temperature
1	$3CaO.Fe_2O_3$.$3SiO_2$ $CaCO_3$ Fe_2O_3 SiO_2	1000°C
3	$CaO.V_2O_3.3SiO_2$ $CaCO_3$ NH_4VO_3 SiO_2	1000°C
9	$3CaO.Cr_2O_3.3SiO_2$ $CaCO_3$ $K_2Cr_2O_7$ SiO_2	1000°C

Compositions of the blends

The blends were prepared by weighing the corresponding quantities of the initial components, mixing homogenizing them. The grinding and homogenization was carried out simultaneous in a planetary mill Pulverisette 6 (Fritsch, Germany). The materials were ground for 1 h at 150 rpm so the particles of each material had sizes by the order of micrometers. The samples were placed in a furnace at room temperature and the final sintering temperature was 1000°C with isothermal period of 2 h.

Photographs of the initial blends and the pigments synthesized are shown in Fig.1.

Fig. 1. Initial blends and sintered pigments - synthesized at 1000°C

Color measurement

Pigments' colors were determined by a tintometer product of the company Lovibond Tintometer RT 100 Colour by spectral method. In the CIELab system the color coordinates were as follows:

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

The color space of the CIELab system is shown in Figure 2.

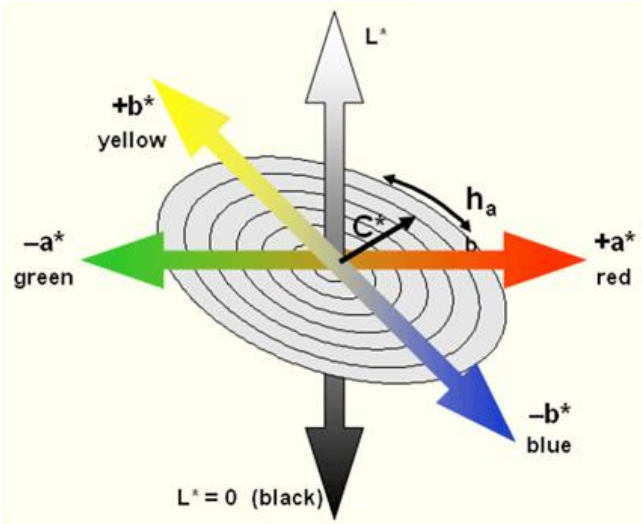

Fig. 2. Colour space of CIELab system

The results obtained from the measuring of the colors of the pigments synthesized are given in Table 2.

Table 2. Results obtained from the measurement of the color coordinates of garnet ceramic pigments in the CIELab system

Sample	Colour	L	a *	b *
1 / 1000°C		62,10	7,53	9,76
3 / 1000°C		90,44	-1,81	11,80
9 / 1000°C		57,97	-4,02	36,14

Infrared spectroscopy

Infrared spectroscopy is vibrational spectroscopic technique used to obtain information about the chemical composition of the sample or its "molecular fingerprint" (Elbakush, A.E. & Güven, D., 2021).

FT-IR spectroscopy is considered to be a fast and cheap method of applied spectroscopy and it shows mainly the information about the absorption peak caused by characteristic fundamental vibrations of some functional groups. The more light of certain wavelength is absorbed, the higher will be absorption peak. If the molecular group of the sample absorbs a number of wavelengths of infrared light then there will be many absorption bands in the IR spectrum recorded. In IR spectra, the position of the band s related to the structure while the zone of the band provides information about the concentrations of specific molecules. Therefore, it can be assumed that the spectrum of the sample reflects its chemical composition (Wang, L. & al., 2021). The IR spectra of the initial mixtures for blends 1, 3 and 9 are shown in Figs.3-5.

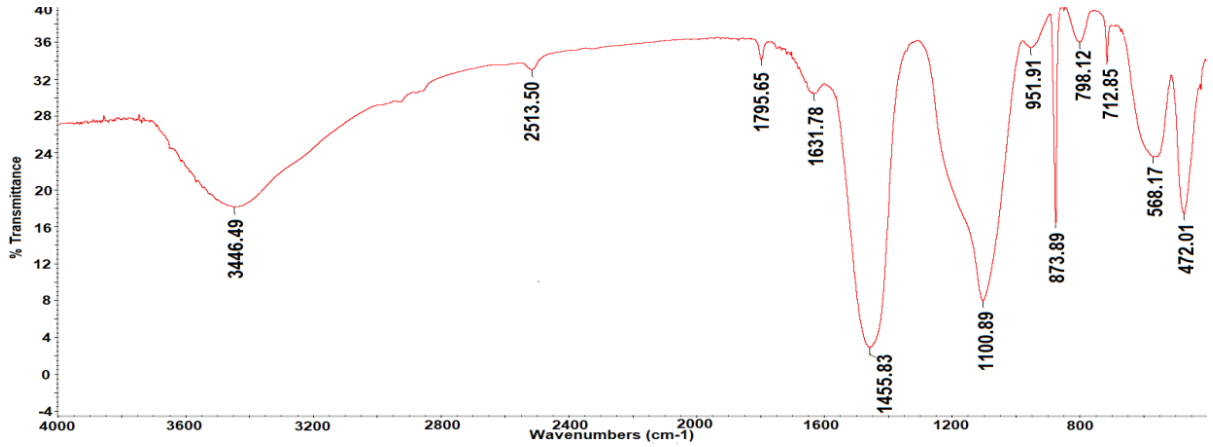

Fig. 3. IR spectrum of blend 1

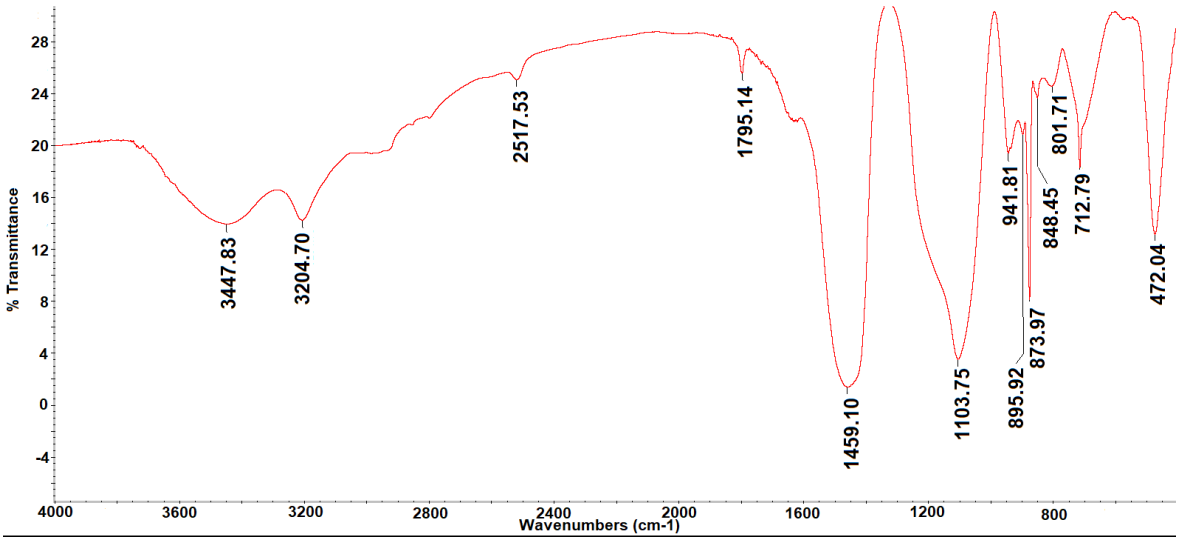

Fig. 4. IR spectrum of blend 3

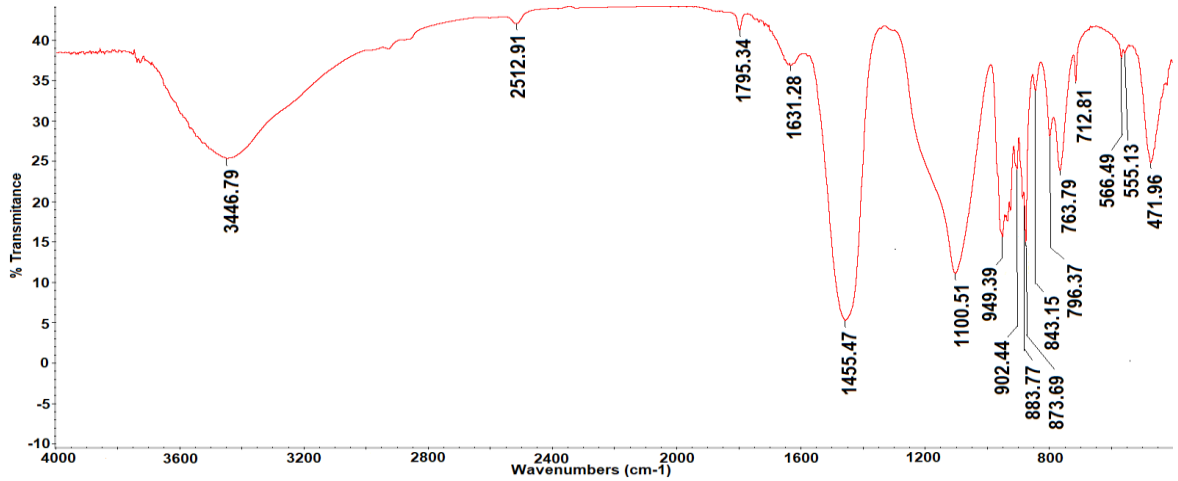

Fig. 5 IR spectrum of blend 9

Figs.6-8 show the IR spectra of blends 1, 3 and 9 sintered at 1000°C.

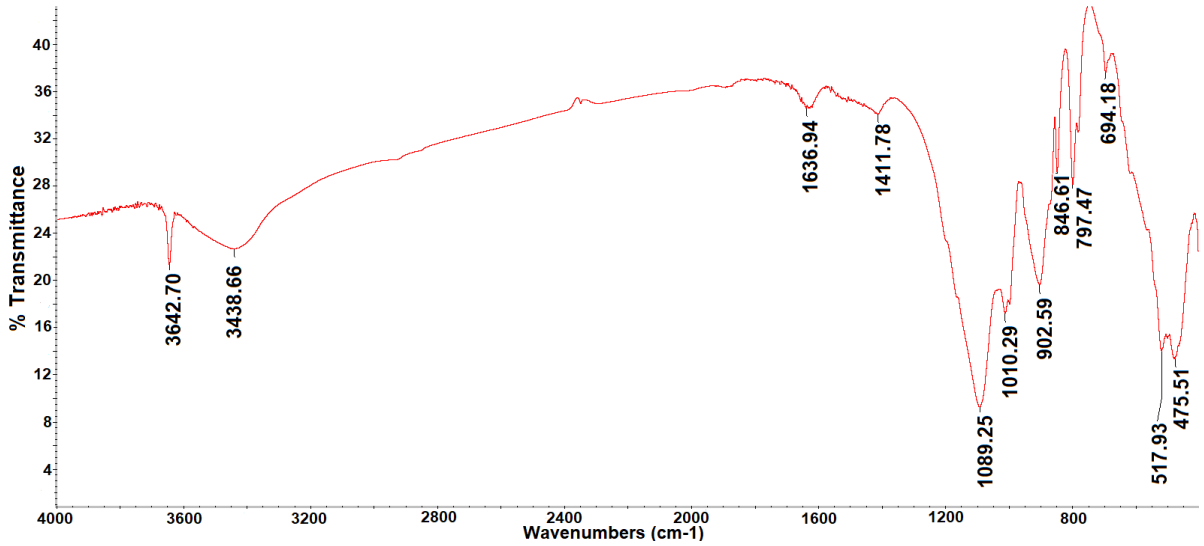

Fig. 6. IR spectrum of blend 1 sintered at 1000°C

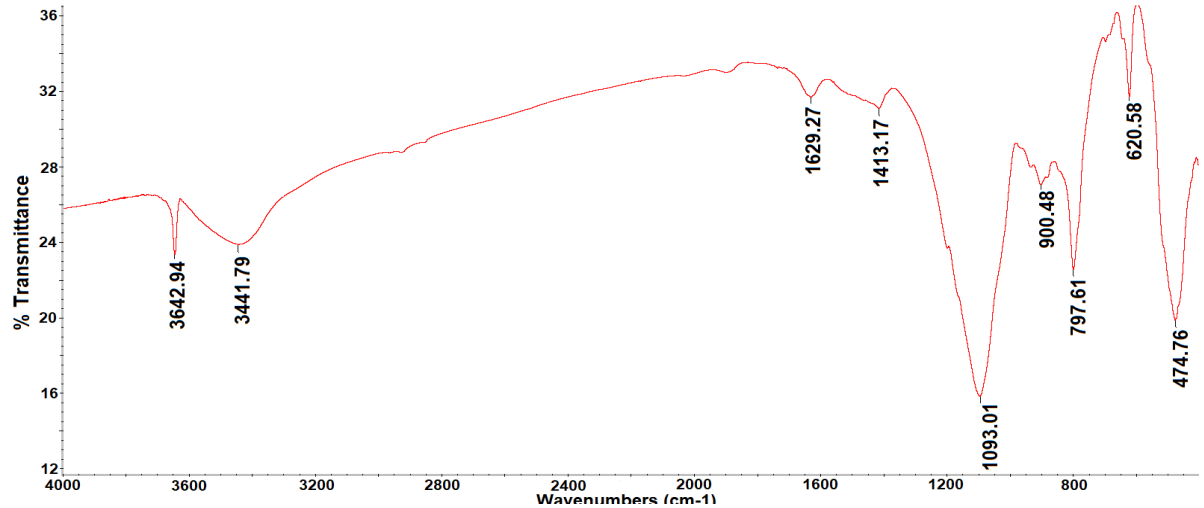

Fig. 7. IR spectrum of blend 3 sintered at 1000°C

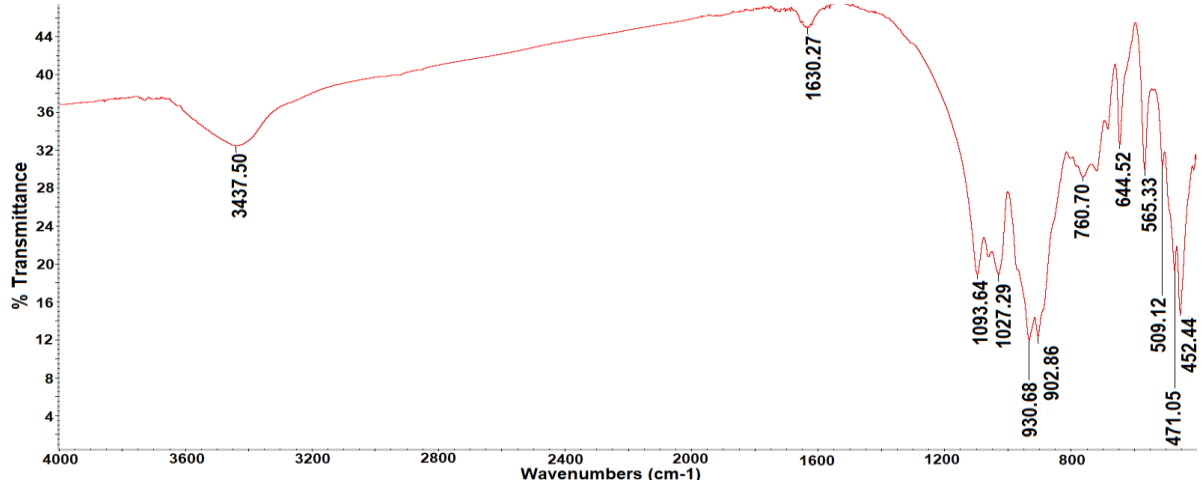

Fig. 8. IR spectrum of blend 9 sintered at 1000°C

The water present in all the samples studied – initial blends and synthesized pigments (Figs.3-8) is represented by the bands in the intervals from 3437.50 to 3447.83 cm^{-1} and from 1629.27 and 1795.65 cm^{-1}. The figures clearly indicate that the amount of water in the sintered pigments was significantly less than that in the initial materials.

The absorption bands at 475.51 cm^{-1} (Fig. 6), 474.76 cm^{-1} (Fig. 7) and 452.44 cm^{-1} (Fig. 8) can be attributed to regimes of stretching or bending vibrations of the O-Si-O and Si-O-Si bonds. The absorption peaks at 694.18 cm^{-1}, 1089.25 cm^{-1} (Fig. 6), 620,58 cm^{-1}, 1093.01 cm^{-1} (Fig. 7) and 644.52 cm^{-1}, 1027.29 cm^{-1}, 1093.64 cm^{-1} (Fig. 8) were attributed to the stretching regimes of Si–O–Si in SiO_4 – tetrahedrons.

During the thermal treatment applied, Ca^{2+} was incessantly absorbed into the silicon network. This in turn resulted in the formation of Si-O-Ca non-bridge oxygen bonds the vibrational regimes of which appeared at 930.68 cm^{-1} (Fig. 8) in the FT-IR spectra of the powders studied. This was linked to the presence of wollastonite in then pigments synthesized (Amin, A.M.M. & al., 2021). In Fig.6, the band at 517.93 cm^{-1} can be attributed to the presence of hematite, in particular to the vibrations of the Fe–O bond in it.

For blend 9 (Fig.8), a band was observed at 565.33 cm^{-1} which can be attributed to the vibrations of the bond Gr–O contained in the mineral uvarovite – $Ca_3Cr_2(SiO_4)_3$ (Parthasarathy, G. & al., 1999).

CONCLUSIONS

Garnet pigments were synthesized from pure oxides by the method of solid state sintering.

The color characteristics of the garnet pigments synthesized were determined using the color measuring system CIELab.

It was established that the garnet pigments synthesized can be used in glazes for faience tiles.

ACKNOWLEDGEMENTS

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