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Obtaining of Ceramic Pigments Suitable forSilicate Industry

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Abstract: This study shows the possibility to synthesis ceramic pigments via solid-state high temperature sintering. The preparation of high temperature ceramic pigments using colourless stable crystal carcasses turns out to be quite suitable method in the case of $ZrSiO_4$ and their colouring by introducing different chromophores. The paper reports for experiments carried out on the synthesis of zircon pigments with the participation of following chromophore ions: Fe^{3+}, Co^{2+}, Ni^{2+} using the technology of solid phase sintering. Many analyses were used to determine the phase composition and check the chromophore ions valency state at temperature higher than the optimal temperature of synthesis. The colour of the pigments was determined using a Lovibond Tintometer RT 100 Color. The willemite ceramic pigments and rice husk ash were studied by X-ray analysis, scanning electron microscopy (SEM). It has been found that the synthesized pigments are suitable and can be successfully applied in glaze tiles and sanitary ceramics.The results obtained indicated that it depends on the sintering temperature isothermal soaking and the type of chromophore ion. In most pigments, the basic phase was obtained as low as 900 - 1000^0C. The best pigments obtained were added to white faience glaze.

Keywords: Ceramic pigments, CIELab color measurement, Oxide additives, Chromophore ions

Introduction

The object of the present study is investigation of possibility of obtaining ceramic pigments by utilizing a widespread bio-waste - rice husks. The use of industrial waste (by-products) as raw materials in the ceramic industry has been under study for decades due to the economical, energy and environmental advantages [1-7]. The combustion of rice husk in air medium results in the production of white rice husk ash (RHA). Rice husk ash contents a high amount of SiO_2 - more than 90% [1]. In our work, as a source of SiO_2, we have used white rice husk ash. Rice husk is waste product containing about 20 % SiO_2. Rice husk is a by-product of rice milling process. Annually, about 500 mln tons of rice are processed to obtain 100 mln tons of rice husk. The latter contain 70-75% organic components and the rest is inorganic components, mainly SiO_2. The use of bio-waste as raw materials in the ceramic industry has been studied for many years due to the economic, energy and environmental advantages.

Ceramic pigments are inorganic colored finely dispersed powders which, when added to some medium, impart certain color and change some of its properties. Beside their coloring ability, the ceramic pigments are resistant to atmospheric and chemical influences, high temperatures, decomposing activity of silicate melts and the effects of light [8-12]. These colored inorganic substances have high coefficient of light refraction, they are insoluble in water, organic solvents and binding materials but possess the ability to disperse in them and impart specific color.

The coloring of the pigment occurs due to the selective absorption of certain wavelengths of light by its crystal lattice. As a result, the pigments are colored in a color complementary to the absorbed one. Most often, the color carriers in the pigments are the chromophores. These are atoms and atomic agglomerates which have the ability to impart one or another color to the substances where they are present.

The ceramic pigments must have the following properties: resistance to high temperatures, resistance to the eroding effects of silicate melts at the temperatures of sintering, high color intensity, cover ability, light stability. Most of the compounds obeying these requirements are colorless. To make them play the role of pigment, they are artificially colored by introducing substances imparting the desired color. Such properties have the compounds of transition d- and f- elements, e.g. vanadium, iron, cobalt, manganese, nickel, chromium, copper, praseodymium, etc. One of the most suitable materials complying with the requirements for pigments mentioned above is willemite. For this reason, it is more and more used for these purposes. Willemite is a mineral – zinc silicate. It has been discovered in the form of small brown crystals and in 1830 was named after the King of Holland Willem I (Willem Frederik). Willemite can be green, yellow, brown, red-brown, orange and blue. It can be found in nature as small prismatic or stubby crystals. It is one of not many silicates with trigonal singony which is more characteristic for the carbonates.

In our earlier studies, we have proved the effect of CoO as an oxide imparting saturated blue color to the willemite pigments [13, 14]. In the present work, the efforts were focused on the effects of other oxides, e.g. NiO and Fe_2O_3, besides CoO, on the synthesis and properties of willemite pigments suitable for the ceramic industry.

Materials and Methods

Materials

The synthesis of pigments is carried out by a solid state reaction using the following chemically pure initial materials: ZnO, CoO, Fe_2O_3, NiO. In thes synthesized pigments ZnO was substituted particularly by CoO, Fe_2O_3, NiO. As a source of SiO_2, white rice husks were used.

Methods

The willemite ceramic pigments and rice husk ash were studied by X-ray analysis, infrared spectroscopy (FT-IR), differential thermal analysis (DTA) and scanning electron microscopy (SEM) as well as by the system of color measurement – CIELab.

The X-ray analyses were carried out by the method of powder diffraction using X-ray apparatus equipped D2 PHASER AXS- Bruker, with Cu anode and K_α emission, (CuKα, λ=1.5406Å). The following operating regime was used during the experiments: current 10 mA and voltage 30 kV.

The FT-IR - studies were performed on a Tensor 27 Fourier infrared spectrophotometer FTIR (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.

The DTA experiments were performed on anapparatus for complex thermal analysis (STA 449 F3 Jupiter), NETZSCH, Germany by heating to 1100°C at a rate of 10°C min^{-1}.
The morphology and microstructure of the rice husk were examined by scanning electron microscopy (SEM). The electron microscope photographs of rice husk were taken using scanning electron microscope “Philips SEM525M/EDAX9900” with attached X- ray microanalyst. The microphotograhps were made in a regime of secondary electrons at acceleration of 20 kV.

Color is one of the most important indicators of pigment quality. Colored substances absorb and convert light rays of a certain wavelength into the visible portion of the spectrum, due to their atomic structure. The CIELab system defines colors not only of ceramic pigments but also of other materials, which indicates that this system is universal and widely used. In the present paper the color determination of the pigments is determined spectrally by a tintometer of Lovibond Tintometer RT 100 Color. The colour measurements were performed using the CIELab method. This method, which is the standard analysis in the ceramic industry, especially for the

ceramic pigments allows to determine the whiteness and colour degree of tiles by measuring the three parameters: *L**, *a** and *b**, where:

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

The color space of the CIELab system is shown in Figure 1.

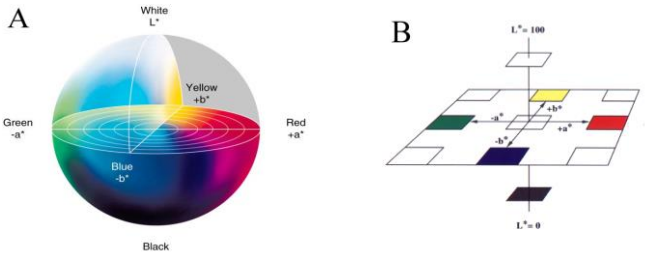

Figure 1. (A,B) The color space of CIELab system

Experiment

Quantities of the starting oxides (ZnO, CoO, Fe_2O_3, NiO) in the 100 g batch recipe are weighed to the nearest 0,1 g, then mixed and homogenized in a PULVERIZETE6 planetary mill of FRITCH. The blends' recipes are calculated as to partially replace ZnO with CoO, Fe_2O_3, NiO in the formation of the willemite. As a source of SiO_2 to the feedstocks, we have added rice husk oxidized at 650°C in air - rice husk ash (RHA). The present study was carried out with rice husk obtained during processing of rice variety Krasnodarski 424 grown in Bulgaria. They are arc-shaped and size approximately: 8 mm length, 2-3 mm width and 0,10÷0,15 mm thickness. The husk contain 74,5% organic matter (cellulose, hemicellulose and lignine) and water, and the rest is inorganic matter containing 20% SiO_2 and 5,5% mixture of the following oxides: CaO, Fe_2O_3, MgO, Al_2O_3, Na_2O, K_2O, MnO_2, as well as traces of Cu and Pb [15-17]. These oxides, accompanying SiO_2 play the role of a mineralizer in the synthesis of pigments.

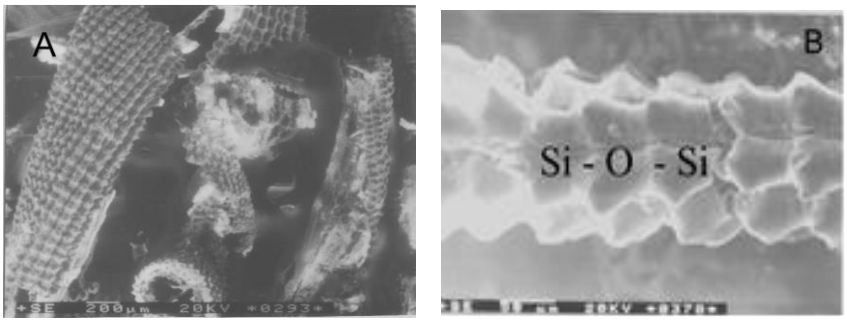

Figure 2. Microphotographs of oxidized rice husk

Figure 2. (A, B) shows images of rice husks burnt in air at greater (Figure 2A) and smaller (Figure 2B) magnification. It can be seen from the two images that mainly inorganic mass forming the silicon-oxygen carcass remains after the removal of the organics. The silicon-oxygen carcass (Si-O-Si) which builds the oxidized husk is clearly seen in Figure 2B.

The synthesis of pigments was carried out by the method of solid state sintering. The sintering of the initial blends, the compositions of which are presented in Table 1., was performed in a laboratory muffle furnace at heating rate 6 ^{o}C\min and 2 h isothermal period at the final temperature. The pigments were sintered at 900^{o}C, 1000^{o}C, 1100°C and 1150°C. After the sintering, additional homogenization was carried out in a planetary mill PULVERIZETE6, product of "FRITCH" Co.

Results and Discussion

Characterization of the blends by DTA

The raw materials mixtures were subjected to differential-thermal analysis to study the processes occurring with them at heating to 1100 °C. Three mixtures prepared for synthesis of pigments were analyzed: C1 and C2, N1 and N2, F1 and F2. The results obtained are presented in Figures 3-5.

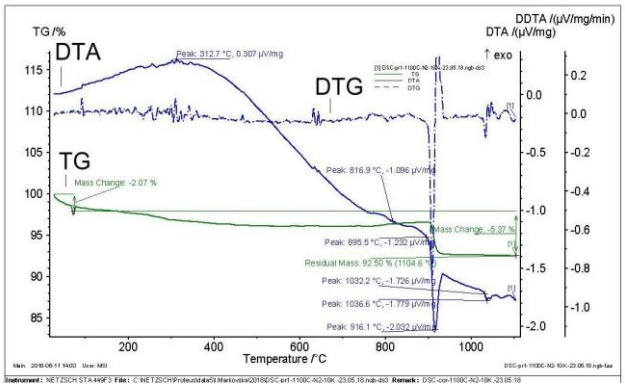

Figure 3. DTA of mixtures for samples C1 и C2
(synthesized at 1000 °C and 1150 °C)

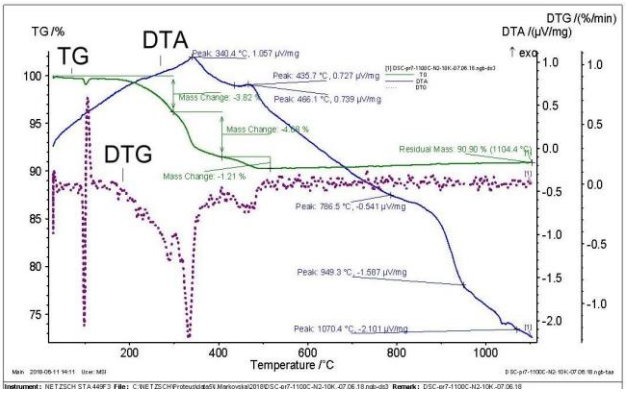

Figure 4. DTA of mixtures for samples N1 and N2
(synthesized at 1000 °C and 1150 °C)

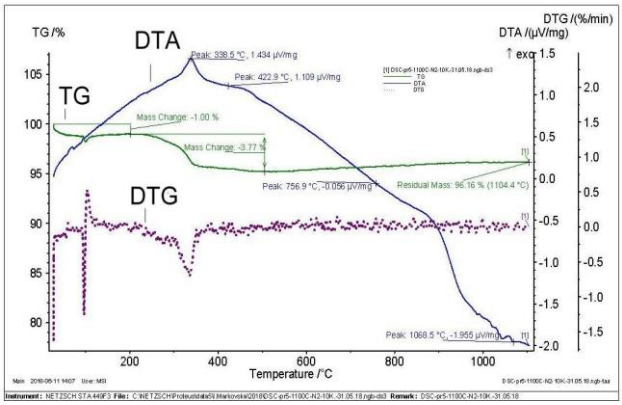

Figure 5. DTA of mixtures for samples F1 and F2
(synthesized at 1000 °C and 1150 °C)

The analysis of the TG curves showed that the biggest mass loss was observed for the mixtures containing NiO (N1 and N2) – 9,1% and the smallest – for mixtures F1 and F2 – 3,84%. The mass loss for the mixtures C1 and

C2 was 7,5 %. The peak observed at 100 ºC was attributed to humidity elimination [18]. Further mass loss can be related to the finished oxidation of the residual carbon of the rice husk and release of volatile components of the rice husks and the mixtures.

Clearly distinguishable exothermal peak was observed in all the DTA curves: at 312 ºC (fig.3), 340 ºC (Figure 4.) and 338ºC (fig.5) which was attributed to the finished oxidation of rice husks residual carbon. Figure 3. shows also a strong endothermic peak at around 920 ºC which was can be connected with the transformation of willemite into cobaltine.

Color Measurement

One of the most characteristic properties of the pigments is their color. In this respect, one of the most important studies of pigments is connected with the determination of their color coordinates. The results obtained for color coordinates of the pigments synthesized from mixtures C1 – C5, F1 – F2 and N1 – N2 were determined in the system CIELab and they are shown in Table 1.

Table 1. Results of color coordinates measurements using CIELabe system

№ sample	Composition	Color	T ,ºC	L*	a *	b *
C1	$CoO.ZnO.SiO_2$		1000	31,50	-3,35	-9,50
C2	$CoO.ZnO.SiO_2$		1150	28,25	3,03	-17,74
C3	0,375 $CoO.1{,}625.ZnO.SiO_2$		900	35,82	-6,93	-14,26
C4	0,375 $CoO.1{,}625.ZnO.SiO_2$		1000	35,68	2,08	-41,24
C5	0,375 $CoO.1{,}625.ZnO.SiO_2$		1100	34,70	10,72	-39,08
F1	$Fe_2O_3.ZnO.SiO_2$		1000	53,14	23,23	44,16
F2	$Fe_2O_3.ZnO.SiO_2$		1150	35,91	14,12	17,17
N1	$NiO.ZnO.SiO_2$		1000	69,86	-3,94	21,62
N2	$NiO.ZnO.SiO_2$		1150	63,29	-13,75	15,97

It can be seen from the data presented that the best results were obtained by the synthesis of the Co-willemite pigments. The most saturated color had the pigment with composition C4 (0,375CoO.1,625ZnO. SiO_2) sintered at 1000 ^oC where the amount of blue color measured in the CIELab system was b*= -41.24. The results shown in Table 1. indicated that the optimal temperature for synthesis of cobalt-willemite pigments is 1000 ^oC.

The pigments synthesized which contained iron – mixtures F1 and F2 had brown color with the values of the coordinates a* and b* decreasing with the increase of the sintering temperature – they were a* - 23,23 and b* - 44,16 at 1000 ºC and a* - 14,12 and b* -17,17 at 1100 ºC.

The color observed for the nickel-willemite pigments was green and the amount of green color increased with the increase of the sintering temperature (-a*) while parameter (+b*) decreased.
A tendency of decrease of luminance L* was observed for all the pigments (they became darker) with the increase of the sintering temperature.

X - ray Analysis

The X–ray analysis carried out showed that cobalt-willemite ceramic pigments were synthesized in the system $x.CoO.(2-x).ZnO.SiO_2$, where x=0,375 and 1,00, as well as nickel-willemite ceramic pigments in the system $NiO.(2-x).ZnO.SiO_2$, where x=1,00 (Figures 6-9). The addition of iron resulted in synthesis of spinel pigments containing smaller amounts of willemite. (Figure 8.). The results shown in Figures6-9 correlate excellently with these for color and luminance presented in Table 1.

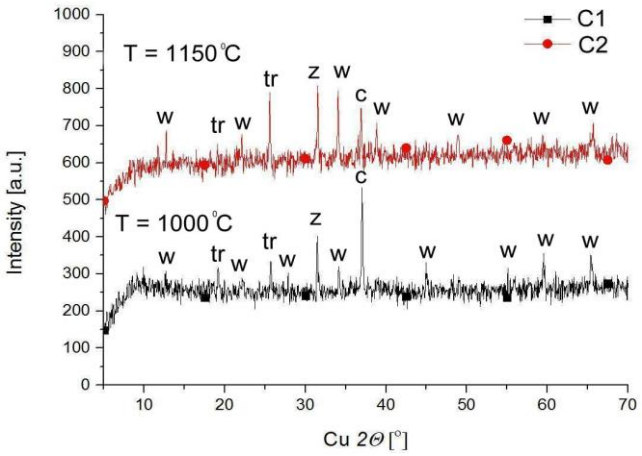

Figure 6. XRD parents of Co - dopped zinc silicate annealed at 1000 and 1150 °C. Legend: w- willemite, tr- trydimite (SiO_2), z- ZnO, c- CoO

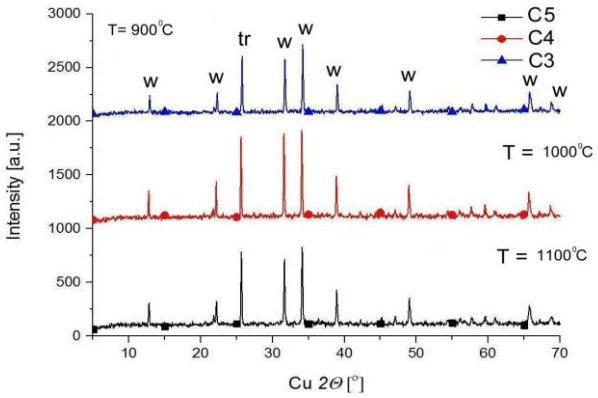

Figure 7. XRD parents of Co - dopped (0,375CoO) zinc silicate annealed at 900, 1000 and 1100 °C. Legend: w- willemite, tr- trydimite (SiO_2)

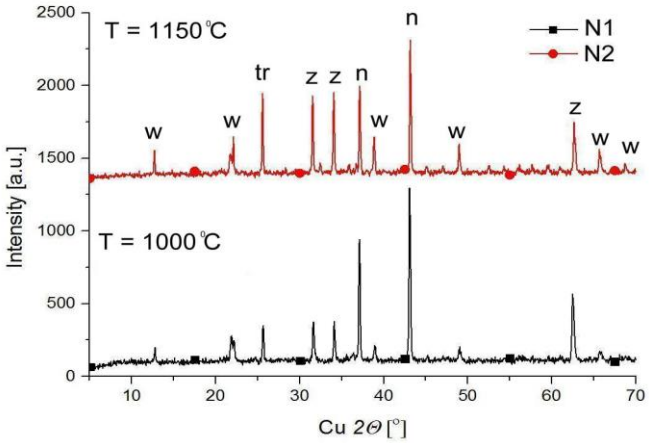

Figure 8. XRD parents of Ni - dopped zinc silicate annealed at 1000 and 1150 °C. Legend: w- willemite, tr- trydimite (SiO_2), z- ZnO, n - NiO

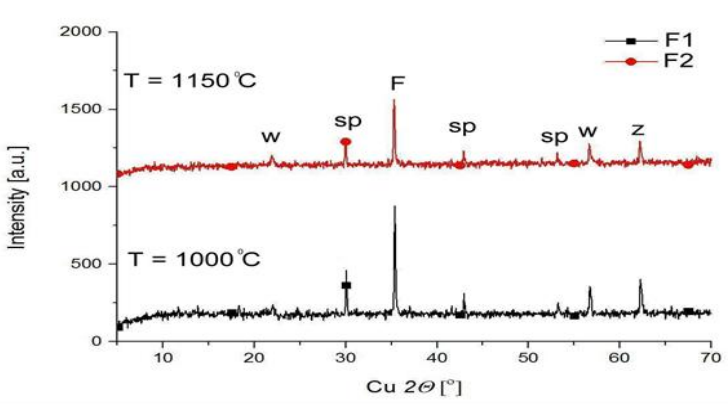

Figure 9. XRD parents of Fe - dopped zinc silicate annealed at 1000 °C and 1150 °C. Legend: w- willemite, sp– spinel ($ZnO.Fe_2O_3$), z- ZnO, f- Fe_2O_3

The diffraction patterns shown above (Figures 6-9) indicated that it is possible to obtain willemite pigments by substitution of ZnO with CoO and NiO. It can be concluded fom the four figures that the best results were obtained for the mixtures with 0,375 CoO – C3÷C5. The powder heated at 900 ^{0}C, 1000 ^{0}C and 1100 ^{0}C consisted mainly of crystalline Zn_2SiO_4 (willemite). X- ray data shows that the quality of Zn_2SiO_4 is achieved at 1000ºC – composition C4 (Figure 7.). This fact is confirmed by the work of T. Pangilinan-Ferolin and R. Vequizo [19] who studied the synthesis of zinc silicate by solid-state reaction using silica from rice husks ash (RHA). In mixture C4 sintered at 1000 ºC, obviously, complete substitution of zinc by cobalt in the crystal lattice of zinc silicate was achieved to form willemite-cobaltine and this is the reason for the better values determined by the measurement of color coordinates of the pigments (b*= -41,24 and L*= 39,08). Significant amount of cobaltine was obtained with the mixtures containing 1 mole CoO but the color coordinates measured were worse than these for the compositions with 0,375 CoO.

By the addition of BiO in the initial mixture, a weaker interaction was observ3d between ZnO and SiO_2 from the rice husks and, respectively, less zinc was substituted by nickel in willemite lattice (Figure 8.).

The smallest amount of willemite was obtained by the addition of Fe_2O_3 to the initial mixtures. In this case, Fe_2O_3 bonds predominantly with ZnO to form a new compound – chemically bonded spinel $ZnO.Fe_2O_3$ (Figure 9.). Most probably, the reason for this was preservation of the electroneutrality of the lattice.

In the system Fe_2O_3 - ZnO - SiO_2, practically brown spinel pigments with very good characteristics were obtained. Better color characteristics had the pigments synthesized at 1000°C – mixture F1 (b* =44,16, L*=53,14). With this composition, the amount of the spinel phase predominates the willemite phase (Figure 8.). The works of Masslennikova et al. confirm our results for Ni and Fe doped pigments [20-21]. By the high temperature sintering of the four initial mixtures, beside the newly formed chemical compounds – willemite or spinel, remain unreacted initial oxides the peaks of which can be observed in the diffraction patterns. The results obtained from the XRD analysis showed that almost all of the SiO_2 from the rice husks reacted with ZnO in mixtures C1 – C5, N1 and N2 to give willemite, while in mixtures F1 and F2 (Figure 9.) SiO_2 binds to ZnO mainly before the formation of spinel - $ZnO.Fe_2O_3$ so the willemite synthesized was less. It can be seen in all the four Figures 6 -9 that due to the presence of alkali impurities in the rice husks (Na_2O, K_2O), the high temperature modification of SiO_2 was α- tridymite but not α- cristobalite, as it usually occurs in practices.

FT-IR Analysis

Three kinds of pigments synthesized at 1150ºC and containing: CoO (composition C2), NiO (composition N2) and Fe_2O_3 (composition F2) were subjected to FT-IR analysis. The FT-IR spectra of $Zn_{2-x}Co_x$ SiO_4, $Ni_{2-x}Co_x$ SiO_4, and Fe- Zn spinel pigments sintered at 1150 ^{0}C are shown in Figures 10-12.

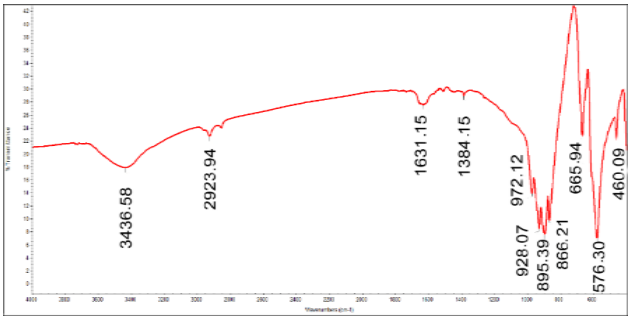

Figure 10. FTIR spectrum of composition C2 ($CoO.ZnO.SiO_2$)

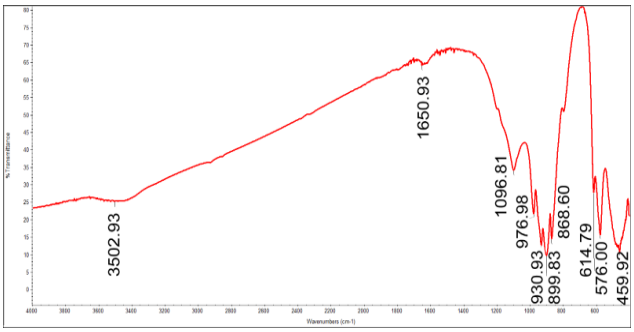

Figure 11. FTIR spectrum of composition N2 ($NiO.ZnO.SiO_2$)

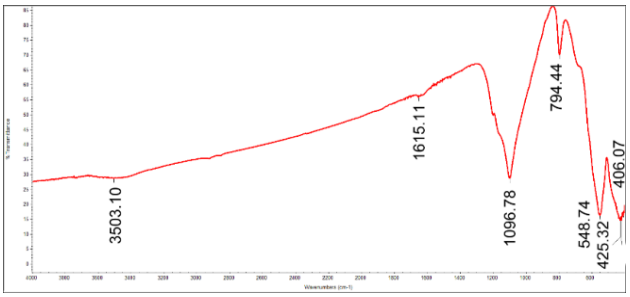

Figure 12. FTIR spectrum of composition F2 ($Fe_2O_3.ZnO.SiO_2$)

The weak absorption bands present in all the three spectra with maximum at about 3436 - 3500 cm^{-1} can be attributed to the valent vibrations of the OH bond in the water molecules with hydrogen bonds. The weak absorption band at 1631,15, 1650,93 and 1615,11 cm^{-1}, resp., results from the deformation vibrations of the water molecules (δ-H_2O) [16]. The intense band at 1096.81 cm^{-1}, resp. 1096,78 cm^{-1}, was due to the valent vibrations of the silicon-oxygen tetrahedrons - ν_{as} (SiO_4). The characteristic bands at 976,98 cm^{-1}, respectively 972,12 cm^{-1}; 928,07 cm^{-1}, respectively 930,93 cm^{-1} and 895,39 cm^{-1}, respectively 899,83 cm^{-1} corresponds to asymmetric stretching vibration modes as (SiO_4) [22]. The characteristic bands at 866,21 cm^{-1}, respectively 868,60 cm^{-1}, and the presence of an absorption band at 794 cm^{-1} can be explained by symmetric stretching vibration (s) of Si-O bonds from silicon-oxygen tetrahedra (SiO_4). The two vibrations at 576,30 cm^{-1}, respectively 576,00 cm^{-1} and 614,79 cm^{-1}, characterize the willemite structure and probably correspond to the asymmetric modes of vibrations (vas ZnO_4) and symmetric (vsZnO_4) [22].

The existence of absorption bands in the low-frequency part of the spectra at about 460/459,92 cm^{-1} can be attributed to the deformation vibrations (δ_{as}) of the bonds Si – O in the SiO_4, tetrahedrons, as well as to the symmetric stretching vibration of ZnO_4 (νZnO_4) [16,22].

Conclusion

The possibility to synthesize willemite pigments by substitution of ZnO with CoO and NiO: $Zn_{2-x}Co_x$ SiO_4 and $Ni_{2-x}Co_x$ SiO_4 was proved. It was found that the best results were obtained with the cobalt doped pigment with composition C4 ($0{,}375CoO.1{,}625ZnO.SiO_2$) synthesized at temperature of 1000 ^oC.

In those case, zinc was totally substituted by cobalt in the crystal lattice of the zinc silicate to form willemite-cobaltine and this stipulates the better result obtained by the measurement of the color coordinates of the pigments where the amount of blue color measured in the system CIELab was b* =-41.24. The same composition showed also the highest luminance (L* =39,08) and saturation of the color.

The XRD analyses indicated that the addition of NiO to the initial mixture leads to worse substitution of zinc by nickel in the willemite lattice so the amount of willemite formed was less. The pigments synthesized had green color.

By the addition of Fe_2O_3 resulted in simultaneous synthesis of willemite and iron-zinc spinel where the Fe-Zn spinel ($ZnO.Fe_2O_3$) predominated. At temperature of synthesis 1000^oC, the spinel phase was the biggest one and pigments were colored in light-brown. The optimal parameters for the process of synthesis of all the initial mixtures were established. The synthesized pigments are suitable and can be successfully applied in glaze tiles and sanitary ceramics.

Acknowledgements

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