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# Synthesis and characterization of ceramic pigments in the system $CaO.NiO.MgO.2SiO_2$

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For the preparation of ceramic pigments in the system $CaO.NiO.MgO.2SiO_2$, the starting compositions are determined from the basic mineral diopside following the expression $CaO.xNiO.(1\text{-}x)MgO.2SiO_2$, where x = 0.1, 0.3, 0.5, 0.7 and 0.9. Ceramic pigments were synthesized via solid-state high temperature sintering. Starting materials used for the synthesis are $CaCO_3$, NiO, 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 1 hour at the final temperature. The resulting powder mixtures were sintered at 1000, 1100 and 1200°C in order to obtain Ni-doped diopside.

*X-ray diffraction (XRD) analysis:*

The powder XRD data revealed that the ceramics synthesized at different temperature and Ni concentration vary in their phase composition. X-ray diffraction patterns of the synthesized ceramic pigments are shown on Fig. 1. and Fig. 2. As it is seen the intensity of diopside peaks increases with increase of temperature. The most crystalline diopside is obtained at 1200°C. Some of the low intensity peaks, marked with asterisk, reveal presence of minor amount of nickel and magnesium oxides in samples sintered at 1000 and 1100°C. Such phases disappeared at 1200°C temperature of sintering for 0.1NiO sample with low nickel, but remain for 0.3NiO. These phases increase for samples with higher concentration of Ni. At the same time, the absence of nickel oxide in the sample 0.1NiO sintered at 1200°C indicates indirectly that Ni enters the diopside lattice, as this is the predominant phase for this composition. Diopside phase prevail in samples with 0.1 and 0.3NiO content in the initial batch. Wollastonite is presented in all studied samples, prevailing over diopside at higher nickel concentration.

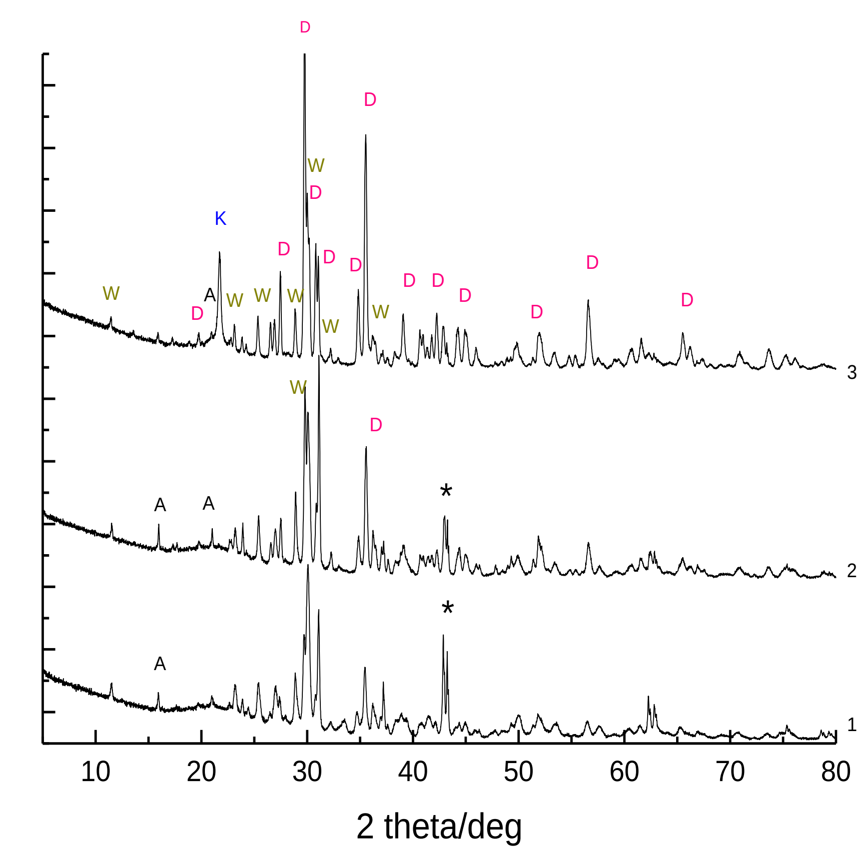


**Figure 1.** Powder XRD patterns of synthesized pigments in the system $CaO.0.1NiO.0.9MgO.2SiO_2$ at different temperatures (1-1000°C; 2-1100°C; 3-1200°C): D - Diopside, W - Wollastonite, A - Åkermanite, K - Crystobalite, * - MgO; NiO

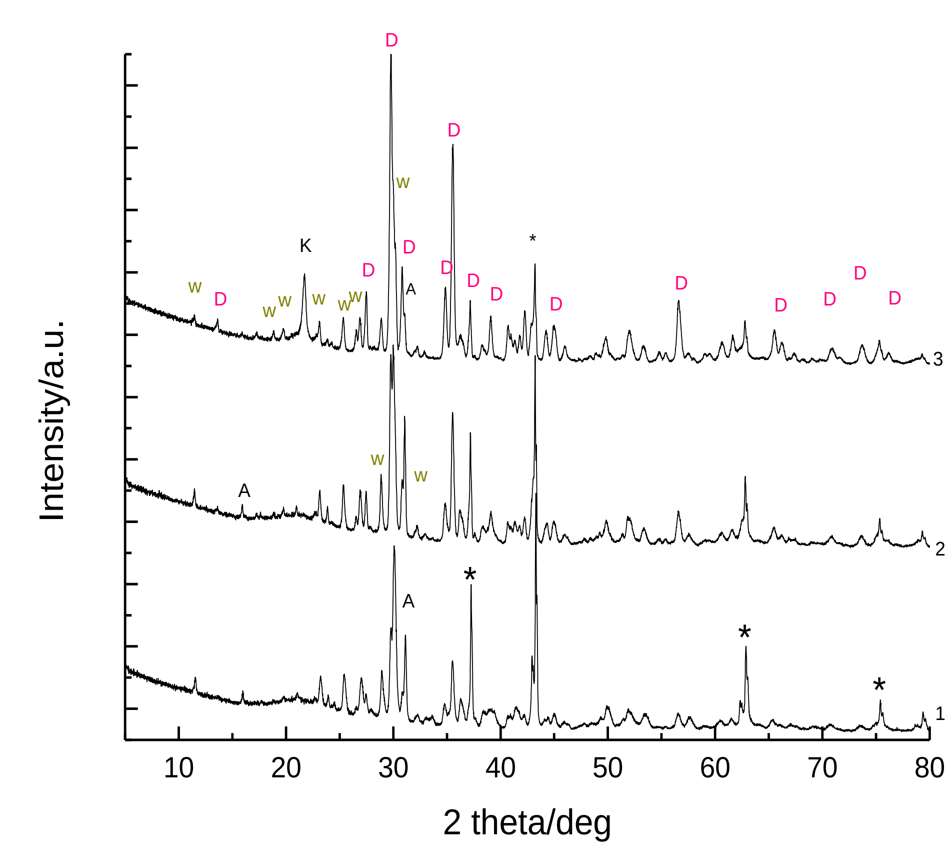


**Figure 2.** Powder XRD patterns of synthesized pigments in the system $CaO.0.3NiO.0.7MgO.2SiO_2$ at different temperatures (1-1000°C; 2-1100°C; 3-1200°C)D - Diopside, W - Wollastonite, A - Äkermanite, K - Crystobalite, * - MgO; NiO

**Table 1.** Infrared peaks position and assignment compared to diopside reference s-strong; b- broad

| Observed infrared peaks | Diopside peak positions according [12] | Assignment |
|---|---|---|
| **411** | 395 | O-Ca-O bending<br>Chain deformation |
| **510 (s)** | 510 | O-Mg-O bending<br>Chain deformation |
| **636** | 630 | O-Si-O bending |
| **676-686** | 670 | |
| **~880 (b)** | 865<br>920 | Si-O stretching |
| **967-963 (s)** | 965 | Si-O stretching |
| **1072 (s)** | 1070 | |

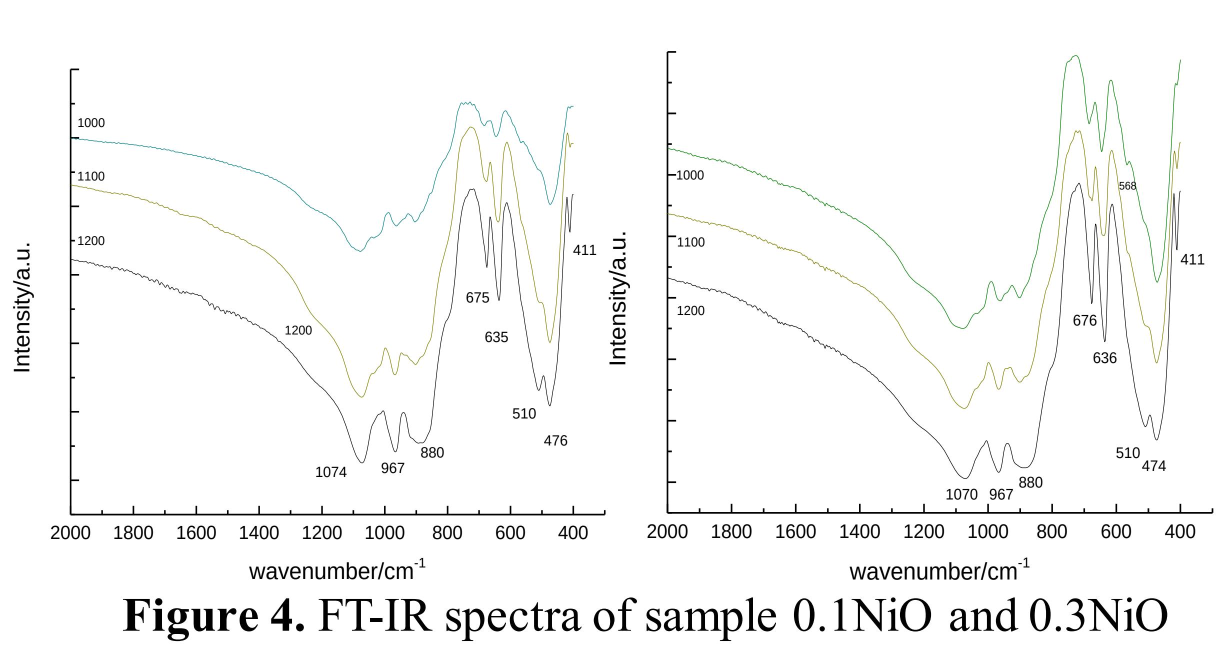


**Figure 4.** FT-IR spectra of sample 0.1NiO and 0.3NiO

The results obtained for colour coordinates of the pigments are shown that the colour of the synthesized ceramics is light green. As the heating temperature increases, an increase in L * (except for the composition by 0.1NiO) is observed. The amount of green colour (-a *) is greatest (-a * = -8.5) in the pigment with composition $CaO.0.3NiO.0.7MgO.2SiO_2$, synthesized at 1200ºC.

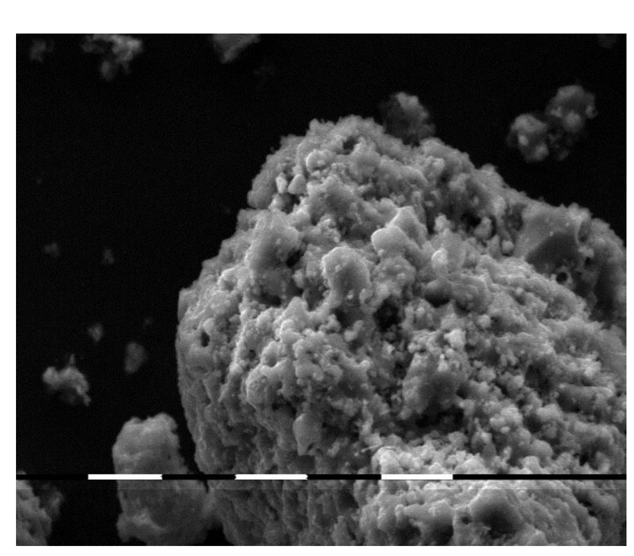

**Figure 3.** SEM images of ceramics 0.1NiO

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 1200°C (Figure 3) samples with different nickel content reveal that powder sample is composed of dense aggregates.

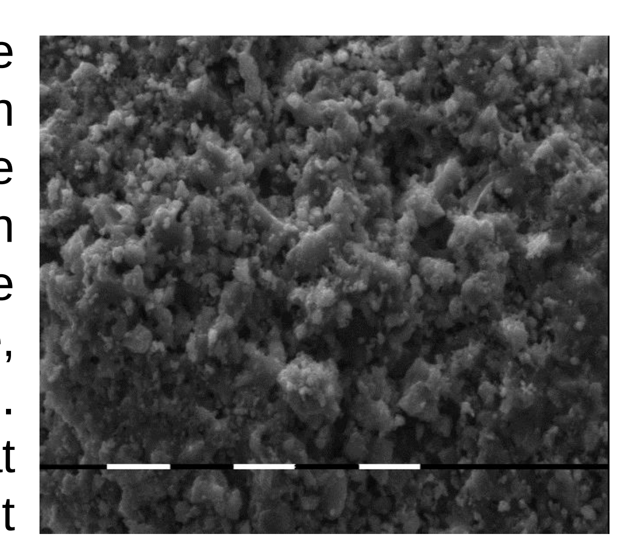

**Figure 3A.** SEM images of ceramics 0.3NiO

Colour is one of the most important indicators of pigment quality. Coloured 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 CIELab system, the colour coordinates are:

-L* (brightness), from absolute white L* = 100 to absolute black L*=0

-a* - green colour ( - ) / red colour ( + ) -b* - blue colour ( - ) / yellow colour ( + )

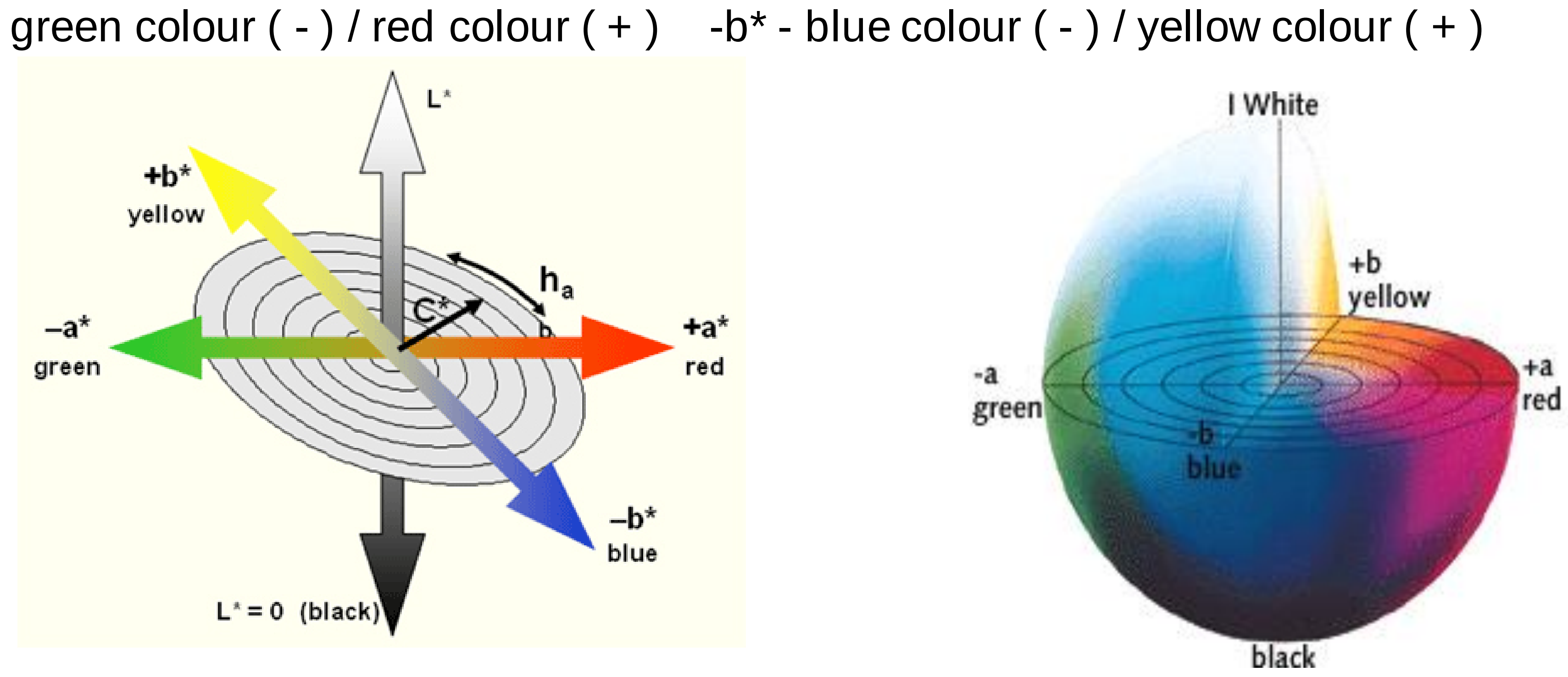


**Figure 5.** The colour space of CIELab system

## Conclusions

Light green ceramic pigments were synthesized on the basis of diopside by the method of solid phase sintering. The optimal parameters for synthesis of nickel dopped, predominantly diopside containing ceramics were determined. The best results for the green component in colour were obtained with the pigment 0.3 NiO synthesized at sintering temperature of 1200˚C.