# Elaboration and characterization of Co-$Zn_2SiO_4$ pigments

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In this communication, we reports results on the synthesis of $Zn_{2-x}Co_xSiO_4$ ($0 \leq x \leq 1$) ceramic pigments by sol-gel method with the main aim of achieving high purity at lower temperatures. The second objective is to obtain a variety of colours (turquoise, purple, violet and blue) with a minimum quantity as possible as of cobalt. The materials were investigated by X-ray diffraction, infra-red spectroscopy, UV-visible spectroscopy, Lab-colour measurements and Scanning Electron Microscopy (SEM).

## I. INTRODUCTION

Except the turquoise-blue pigments of vanadium-zircon, which presents reproducibility problems in industrial conditions, the current used source of blue colour in ceramic pigments is cobalt. The major compounds used are $Co_2SiO_4$, $Co_2SnO_4$ and $CoAl_2O_4$. These pigments occurs the intense blue colour but they contains a high quantity of cobalt. Nowadays, the cobalt is expensive and considered to be a toxic element. Thus, its introduction in chemically and thermally stable crystalline matrix such as $Zn_2SiO_4$, $ZrSiO_4$ and $ZnAl_2O_4$ proves to minimise these problems: cost and toxicity.
The willemite has attracted interest as a host lattice for the incorporation of colourant ions such as $Co^{2+}$ and $Ni^{2+}$ and luminescent ions such as $Mn^{2+}$, $Eu^{3+}$ and $Tb^{3+}$ [1-4].

## II. EXPRIMENTAL

The Co-doped willemite ($Zn_{2-x}Co_xSiO_4$) pigments were synthesised using the sol-gel process, from silicic acid ($H_2Si_2O_5$) prepared by ion-exchanged of $K_2Si_2O_5$ on an amberlite resin and an aqueous solution of $Zn(C_4H_6O_4)$ and $CoCl_2,6H_2O$. The mixture was stirred for 24h and refluxed at 100°C. The sol obtained was quickly evaporated and the so-obtained gel dried at 100°C. The ground powders were fired for two hours at 900°C. The nominal compositions of the samples are shown in table I.

The crystalline phase of the pigments was identified by x-ray diffraction and infra-red spectroscopy. UV-visible spectra were obtained in the range between 200 and 1200 nm by the diffuse reflectance method. In addition, the colour parameters (Lab) and chromaticity parameters (xyz) were determined in the 380-780 nm range for a D65 illumination.

| Sample | W0 | W1 | W2 | W3 | W4 | W5 | W6 | W7 | W8 |
|---|---|---|---|---|---|---|---|---|---|
| x | 0.00 | 0.05 | 0.15 | 0.25 | 0.50 | 0.75 | 0.85 | 0.95 | 1.00 |

Table I: the samples prepared ($Zn_{2-x}Co_xSiO_4$) (x: the composition of the initial solution).

## III. RESULTS AND DISCUSSION

Figures 1, 2 and 3 show the XRD, IR and UV-visible spectra of typical samples. The study of the X-ray diffractograms reveals that the willemite started to crystallize at 100°C. The diffractograms of all samples heat-treated at 900°C for 2 hours show that the willemite phase is completely formed. For samples w0 to w4, no second phases were detected indicating that the solid solution $Zn_{2-x}Co_xSiO_4$ is well formed.

The infra-red spectra, in the range 400 to 1500$cm^{-1}$ for some pigments are shown in figure 2. These spectra did not present any significant

 

differences. The bands in the ranges 450 to 600 $cm^{-1}$ and 800 to 1020$cm^{-1}$ are characteristic of the willemite. The bands at 1090 and 1360 $cm^{-1}$ are assigned to Si-O[5]. The band at 660 $cm^{-1}$ is assigned to $Co_3O_4$.

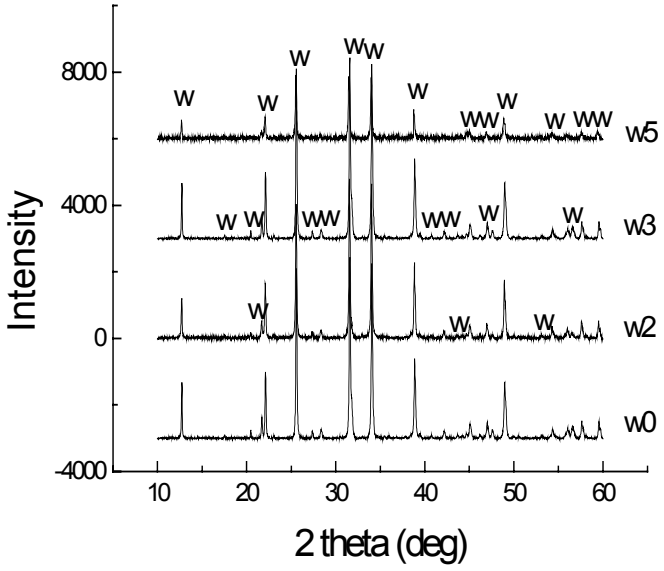


Figure 1: X-ray diffraction of samples heated at 900°C(w = willemite).

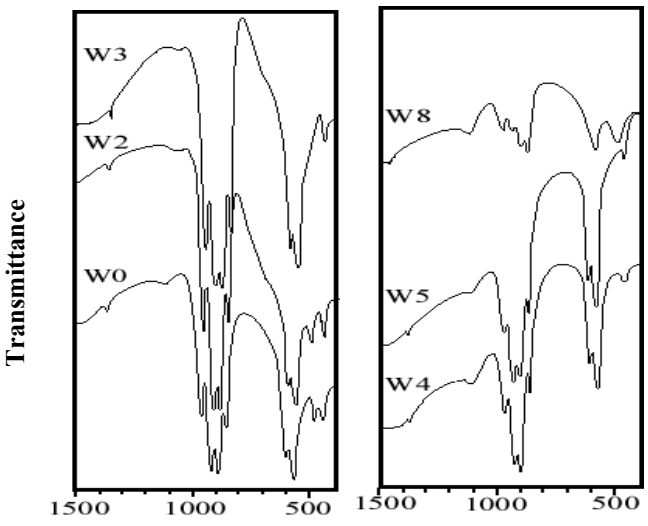


Figure 2: Infrared spectra of pigments calcined at 900°C.

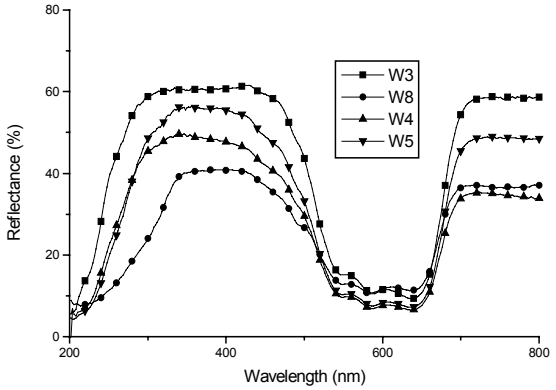


Figure 3: Diffuse reflectance spectra of some samples fired at 900°C.

In the literature[6] the diagram of the energy levels for the cation $Co^{2+}$, with an electronic configuration $3d^7$ in the tetrahedral coordination shows three transitions:

$$\nu_1: {}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$$
$$\nu_2: {}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$$
$$\nu_3: {}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$$

For all samples (figure 2) a broad band in the range 540-630 $cm^{-1}$, which seems to be composed of three different bands (540, 590 and 640 $cm^{-1}$), is due to tetrahedrally-coordinated cobalt and is assigned to the third transition. This assignment is in accordance with results of x-ray diffraction and infra-red spectroscopy; indeed the cobalt was replaced the zinc occupying the tetrahedral sites.

The samples have been observed by SEM (Fig. 4). The morphology of the powder (sample W5) shows grains with a mean size around 1.5 μm. This grain size is useful in pigments colouration.

The diffuse reflectance spectra of figure 3 were used to determine the colour parameters of the various pigments containing different amounts of cobalt calcined at 900°C ((table II). The b values of pigments w1 to w5 decrease with the increasing of cobalt content. The pigment w5 shows the highest value of b. For x≥0.75 (sample w6 to w8) the b parameter increases upon increasing the cobalt amount which can be correlated with the structural modifications.

| Pigment | Colour Parameters | | | | | | R400 | R700 |
|---|---|---|---|---|---|---|---|---|
| | x | y | z | L | a | b | | |
| W2 (x=0.15) | 0.2247 | 0.2590 | 0.5163 | 60.8028 | -9.9151 | -29.578 | 40.26 | 49.44 |
| W3 (x=0.25) | 0.1945 | 0.2010 | 0.6044 | 47.1595 | 1.6348 | -43.876 | 47.70 | 33.71 |
| W4 (x=0.50) | 0.1971 | 0.2096 | 0.5933 | 56.1321 | -1.0643 | -46.643 | 60.64 | 54.29 |
| (x=0.75) | 0.1920 | 0.1940 | 0.6140 | 49.3364 | 3.8485 | -48.1176 | 55.31 | 45.43 |
| W7 (x=0.95) | 0.2263 | 0.2323 | 0.5414 | 49.8155 | 2.3561 | -32.759 | 40.75 | 36.45 |
| W8 (x=1.00) | 0.2277 | 0.2368 | 0.5355 | 49.2960 | 1.0664 | -31.047 | 37.97 | 35.71 |

Table II : Colour parameters and percentage of reflection of pigments fired at 900°C

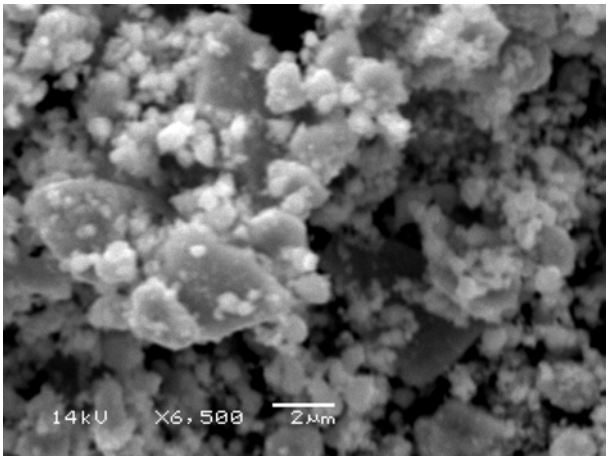


Figure 4: SEM picture of sample W5 .

## VI. CONCLUSIONS

The following conclusions are drawn:

- The solid solutions of Co-$Zn_2SiO_4$ are formed at 900°C, The sol-gel method used in this work allows to obtain the pigments with high purity and relatively at low temperatures,
- A various and intense blue colour with a cobalt addition as well as 35% (mol) are obtained,

These synthesized ceramic pigments are environmentally and economically attractive.

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