$Zn_{2-x}Ni_xSiO_4$ CERAMIC PIGMENTS OF A WILLEMITE STRUCTURE

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In ceramic pigment manufacture, only one ceramic pigment is found in the willemite or phenacite lattice: $(CoZn)_2SiO_4$ blue, code DCMA 7-10-2. On the other hand, cobalt forms an isomorphous blue staining olivine Co_2SiO_4 DCMA 5-08-3 with $NiSiO_4$.

This study presents the synthesis of the mixed pigment $Zn_{2-x}Ni_xSiO4$ with a view to determining the structure and behaviour of the material according to the synthetic method adopted.

The mixed pigment $Zn_{2-x}Ni_xSiO_4$ was obtained by two alternative synthesis procedures, the traditional ceramic method by oxide interdiffusion without using mineralisers (nickel periclase, quartz and zinc oxide) homogenised in a ball mill, and a colloidal sol-gel method with colloidal silica and precursor chlorides. In this method the dissolved or dispersed precursors in the case of colloidal silica, were gelled by controlled ammonia addition to the solution at 70°C with continuous stirring. Gelling occurred at around pH=5.

The powders were heat-treated at 1100°C/6h. Studies were undertaken on the starting microstructures in the unfired materials, determining the arising crystalline phases as well as their crystal cell measurements by X-ray diffraction (XRD) and the UV-V spectrum of the glazed micronised powder in a transparent and in an opaque glaze for porous single-firing.

The results of the XRD characterisation and measurement of the lattice parameters are detailed in Table 1.

The sol-gel specimen developed the olivine as a basic structure with an intense green colour, whereas the ceramic sample developed greenish blue willemite. The result of the glazing was a tendency towards green colours in the ceramic sample and yellow ones in the olivine.

The results indicate the importance of the synthesis method with regard to the final

structure that developed. The XRD characterisation and UV-V spectrum analysis of the materials allowed analysing the position and structure of the materials, revealing the formation of the different types of structures and solid solutions according to the synthesis method employed.

Sample	T(°C)/6h	XRD	ASTM paratemers Zn_2SiO_4 37-1485 Hexag. a=b=13.9381(4) c=9.3100(4) Ni_2SiO_4 37-1485 orthorhomb a=4.725 b=10.118 c=5.908	Measured paratemers
CERAMIC	600	SiO_2(f)NiO(f) ZnO(m) grey		
	900	SiO_2(m)NiO(m) Zn_2SiO_4(mf) blue		
	1,100	SiO_2(m)NiO(m) Zn_2SiO_4(mf) blue		**Zn_2SiO_4** a=b=13.92(2) c=9.32(2)
COLLOID	600	Amorphous light green		
	900	NiO(f) light green		
	1,100	SiO_2(m)NiO(m) Ni_2SiO_4(mf) green		**Ni_2SiO_4** a=4.734(4) b=10.16(2) c=5.94(2)

PEAK INTENSITY: f(strong), m(medium), d(weak).

Table I. *Results obtained.*

With regard to the glaze coatings, the olivine was found to be more unstable and exhibited a lower colour yield than the phenacite, while both presented greenish brown colours.

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