



In situ formation of coloured M(II)-doped Zn_2SiO_4 -willemite in ceramic glazes (M = Mn, Co, Ni, Cu)

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Abstract

The family of M(II) substituted ZnO-wurtzite was investigated as potential new ceramic pigments. When $M_xZn_{1-x}O$ or $(MM')_xZn_{1-x}O$ with (M/M' = Mn, Co, Ni, Cu) oxides are incorporated to industrial frits the development of new colour hues is observed. This is attributed to the in situ formation of coloured M(II)-doped Zn_2SiO_4 -willemite in ceramic glazes. The pigments were prepared by solid state reaction through the traditional ceramic route. Prior to enamelling, the materials were characterized by XRD analysis and FTIR spectroscopy. The colour performance and technological properties of the enamels were evaluated by enamelling in batches containing 5 wt% with a transparent frit, representative of single firing industrial procedures, and submitting them to thermal treatment at 1000 °C. The colours obtained, once the glazes were formed are attributed mainly to the formation of crystalline Zn_2SiO_4 within the glassy matrix, when chromophore M(II) ions enter into the tetrahedral coordination Zn(II) site available in willemite. The colorimetric CIELab parameters measured are in good agreement with the structural and spectroscopic analyses. The colour of some glassy coatings was interpreted by analysing the reflectance UV-visible electronic spectra of the samples. This study demonstrates that this family of pigment is capable of forming its own Zn-based crystals in a conventional transparent ceramic frit giving rise to a wide palette of colours. When Mn, Co, Ni and Cu are present in the Zn(II) site light brown, deep blue, pale yellow and green, are achieved respectively. Furthermore the simultaneous doping with a combination of MM' results in various nice new shades of colours, enlarging the palette of green, yellow, brown and blue hues. The homogeneity of the enamels was confirmed by SEM-EDX microscopy. These materials are promising for ceramic applications since a low amount of pigment would be necessary to achieve intense colouration. © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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1. Introduction

Coloured glazes are mainly produced by adding colouring oxides, most commonly containing iron, copper, cobalt, chromium, manganese, nickel, among other transition metals cations with partially filled *d* or *f* orbitals [1].

Normally the colour of these cations depends on their crystal environment, mainly the oxide anions acting as ligands with a particular geometry. The surrounding oxygen can change the energy of the electronic *d* chromophore levels which yields a

change of colour. In a glaze the colouring is produced by the absorption of certain wavelengths from the chromophore.

Cobalt is a strong colourant that produces a noticeable tint even at concentrations as low as 0.02% CoO and almost all glazes develop blue colour with Co(II) [2]. Indeed all the blue ceramic pigments currently known contain cobalt to some extent when pigment-frit batches are calcined. For instance the substitution of Co(II) at zinc crystal site of the $ZnAl_2O_4$ is currently called gahnite and of the silicate $ZnSiO_4$ [3] is called willemite. Willemite is a traditional commercial blue pigment (DCMA 7-10-2). This crystal lattice is usually preferred for environmental issues because a bluer ceramic pigment is obtained using a lower optimized Co(II) concentration. Normally Co(II) is highly stable at temperatures as high as 1400 °C. In the case of porcelainized bodies the most

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intense and bright blue colour is produced by commercial CoAl_2O_4 (DCMA 13-26-2) [4].

Copper, mainly Cu(II) is also an ancestral colourant giving rise to a wide palette of colours from blue to green and for certain compositions and firing conditions a red hue can be achieved [1,2]. In addition it acts as flux possessing a high solubility in any type of glazes.

Similarly nickel, is mainly as Ni(II) in a variety of shades. Some examples are the Ni/Sb, Nb, Ta yellow and brown rutile pigments, nickel green olivine and Ni/Al commercial spinel [5].

On the other hand Mn exists in multiple oxidation states deriving in different colours depending on composition and firing atmosphere. A pink hue is obtained in oxidizing glazes, on the contrary in reducing atmosphere dark greenish brown shades appear. Usually in ceramic uses Mn is present as MnO_2 . A large amount of this oxide is demanded by the construction industry which uses it in the manufacture of brown, purple, grey and black roof tiles [6]. In the case of the commercial Mn–Al pink corundum, used in the colouring of ceramic bodies, it is difficult to get lot-to-lot reproducibility hues [7].

ZnO, known as zincite, does not contribute any colour but has considerable influence on the colour produced by transition metals. This white oxide is a valuable auxiliary flux in glazes firing up to about 1050 °C. On the other hand ZnO is one of the prototypical functional materials with a variety of applications including catalysts, gas sensors, varistors and thin film-based electronic and electro-optic devices. There are several potential and emerging technical applications of pure or doped ZnO in the field of electronics, optoelectronics. Among them are liquid crystal displays, LED's, spintronics, solar cells, sensors and also in textiles [8]. Due to the electronic and magnetic properties Co-doped ZnO phases are ferromagnetic materials [9] and dilute magnetic semiconductors [10]. Moreover commercial varistors are usually made of a solid solution of ZnO containing transition metal cations and lanthanides [11]. On the other hand nanostructured ZnO novel properties and potential applications have been obtained by the Kirkendall effect for different synthetic procedures [12,13].

In a previous paper the evolution of phases and structural effects caused by the interaction between $\text{Co}_x\text{Zn}_{1-x}\text{O}$ pigments and industrial frits, at different temperatures, has been analysed by XRD and FTIR. This new family of ceramic pigments develops deep blue hue with different frits, transparent and opaque most commonly used in single and double firing procedures. The colorimetric properties of the enamels were analysed by CIELab parameters and UV–visible spectroscopy. According to the electronic spectra the deep blue hue was attributed to the presence of Co(II) in a highly distorted tetrahedral site in the glassy matrix [14]. On the other hand the synthesis of M(II) doped ZnO materials, prepared by combustion synthesis, showing different shades of colours, has been reported [15].

With the aim to produce a new palette of colours this study is extended now to the incorporation of other M(II) chromophores or the combination of MM'(II) in the tetrahedral site available in the ZnO-zincite lattice. One of the main advantages of these doped oxides should be the in situ formation of coloured

$(\text{M}_x\text{Zn}_{1-x})_2\text{SiO}_4$ –willemite by the reaction with the silicate groups from the frit. This incorporation is facilitated by the maintenance of the crystal site occupation during the reaction. A transparent frit commonly applied in single firing procedures in the industry, free of ZnO or other opacifiers, is used in order to evaluate the technological properties of the enamels. In addition some of the pigments were evaluated for their porcelain colouring ability.

2. Experimental details

The $\text{M}_x\text{Zn}_{1-x}\text{O}$ and $(\text{MM}')_x\text{Zn}_{1-x}\text{O}$ pigments were prepared using the traditional ceramic procedure. Mixtures of Mn (CH_3COOH)₂ (Merck 99.9%), CoCO_3 (Aldrich, 99.99%), basic NiCO_3 (BDH 99%), CuO (Riedel-de Haën 99%) and ZnO (Merck, 99%), in stoichiometric proportion, were employed as starting materials for the pigment preparation. The nominal composition of the samples is shown in Table 1.

The starting mixtures were homogenized in an agate mortar and fired in platinum crucibles in a muffle electrical furnace for 2 h, with intermediate grindings. The heating rate was 10 °C/min and the pigments were calcined at 1000 °C. Reactions were carried out in air.

The synthesized mixed oxides were studied by XRD and FTIR analysis. X-ray diffraction patterns were obtained using a Philips PW 3710 diffractometer equipped with graphite monochromator, using $\text{CuK}\alpha$ radiation, and operating at 40 kV and 20 mA. The following x-ray data collection details were applied: slit: divergence:1/12°, receiving slit: 0.2, step interval: 0.02°, and time per step: 1 s.

The infrared spectra were recorded on a Nicolet-Magna 550 FT-IR instrument, using the KBr pellet technique. Unit cell parameters were obtained using a least-square procedure and refined with a locally modified version of the Werner PIRUM programme [16]. The XRD measurements were calibrated using Si as an internal standard.

The pigment and ceramic frit test specimens were prepared by mixing thoroughly. The composition of the transparent frit, typically employed in the single firing process in roof and floor

Table 1
Pigments and their colours.

Pigments	Colours of pigments
$\text{Mn}_x\text{Zn}_{1-x}\text{O}$ ($x=0.02, 0.05$)	Dark yellow
$\text{Co}_x\text{Zn}_{1-x}\text{O}$ ($x=0.02, 0.05, 0.1, 0.2$)	Bright green
$\text{Ni}_x\text{Zn}_{1-x}\text{O}$ ($x=0.02, 0.05, 0.1, 0.2$)	Pale yellow
$\text{Cu}_x\text{Zn}_{1-x}\text{O}$ ($x=0.01, 0.05, 0.1, 0.2$)	Pale green
$(\text{Mn}_{0.01}\text{Co}_{0.01})\text{Zn}_{0.98}\text{O}$	Light green
$(\text{Mn}_{0.025}\text{Co}_{0.025})\text{Zn}_{0.95}\text{O}$	Green
$(\text{Mn}_{0.01}\text{Ni}_{0.01})\text{Zn}_{0.98}\text{O}$	Yellowish green
$(\text{Mn}_{0.015}\text{Ni}_{0.015})\text{Zn}_{0.97}\text{O}$	Yellowish green
$(\text{Mn}_{0.025}\text{Ni}_{0.025})\text{Zn}_{0.95}\text{O}$	Greyish green
$(\text{Mn}_{0.15}\text{Ni}_{0.05})\text{Zn}_{0.8}\text{O}$	Brownish green
$(\text{Co}_{0.01}\text{Ni}_{0.01})\text{Zn}_{0.98}\text{O}$	Bright light green
$(\text{Co}_{0.015}\text{Ni}_{0.015})\text{Zn}_{0.97}\text{O}$	Bright light green
$(\text{Co}_{0.025}\text{Ni}_{0.025})\text{Zn}_{0.95}\text{O}$	Pure green
$(\text{Cu}_{0.01}\text{Mn}_{0.01})\text{Zn}_{0.98}\text{O}$	Mustard yellow
$(\text{Cu}_{0.01}\text{Co}_{0.01})\text{Zn}_{0.98}\text{O}$	Bright green
$(\text{Cu}_{0.01}\text{Ni}_{0.01})\text{Zn}_{0.98}\text{O}$	Light green

Table 2
Approximate composition of transparent ceramic frit in oxides (wt%).

Óxides	(wt%)
Na ₂ O	4–7
K ₂ O	1–3
CaO	3–5
PbO	–
ZnO	–
B ₂ O ₃	14–17
Al ₂ O ₃	9–11
SiO ₂	60–65
ZrO ₂	–

tiles manufacturing, is detailed in Table 2. The mixtures containing 5% pigment were homogenized in an agate mortar. Every bath was wet mixed and the slip was spread on porous ceramic tiles, then dried in air and finally submitted to thermal treatment. In some cases cylindrical test specimens were formed by pressing at 416 MPa the powder containing 0.06 kg H₂O/kg dry solid. The resulting materials were put onto ceramic biscuits and fired. The thermal cycles consisted of heating up to 1000 °C at 25 °C/min, keeping this temperature for 1 h. The pure frit was fired also at different temperatures for comparative purposes.

In addition some pigments were also enamelled on typical porcelainized whiteware or *porcellanato* with weight ratio 1:5. In this case the specimens were fired up to 1200 °C.

All the samples were milled and characterized by XRD and FTIR.

UV–visible spectroscopy measurements of powdered enamels were obtained by diffuse reflectance with a Shimadzu UV-300 instrument model using MgO as a standard.

CIE $L^*a^*b^*$ colour coordinates of coated tiles were obtained with a Braive Super Chroma 20 mm colorimeter and a white standard as reference.

The microstructure of the glassy enamelled tiles was obtained by scanning electron microscopy (SEM) using a Carl Zeiss model MA10 microscope. The x-ray dispersive microanalysis was performed by EDS Orford equipment model INCA Energy. The microstructure of the enamels was obtained on superficially polished gold-coated specimens.

3. Results

3.1. XRD and FTIR structural and spectroscopic characterizations of M(II)–ZnO pigments

The structure of M(II) doped ZnO samples was investigated by XRD analysis and a typical example is shown in Fig. 1. As can be seen the pattern displays the diffraction lines belonging to zincite (ZnO) with wurtzite-type structure (ZnS). The XRD powder patterns of the synthesized oxides could be indexed based on the hexagonal zincite structure, PDF#361451. This indicates that the colourless ZnO-zincite structure is not distorted on substitution of small amounts of M(II) chromophores for Zn to generate pigments, as already observed [15,17]. Very low intensity peaks of NiO were

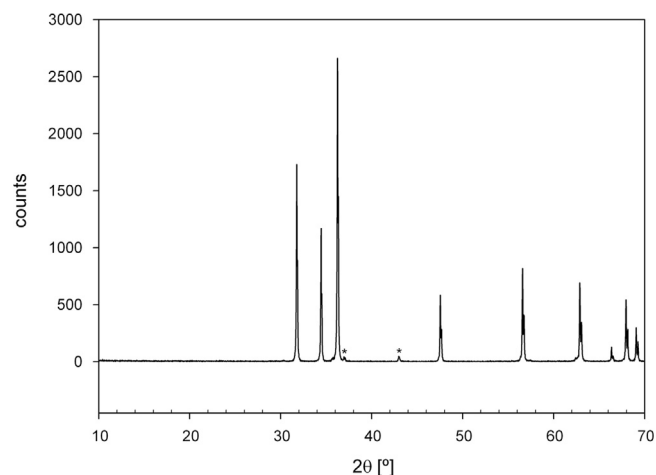


Fig. 1. XRD pattern (Ni_{0.01}Mn_{0.01})Zn_{0.98}O. * Impurity peaks belonging to NiO (# 44-1159).

Table 3
Unit cell parameters and cell volumes of some representative materials.

Pigments	a [Å]	c [Å]
ZnO	3.246(9)	5.201(7)
Ni _{0.02} Zn _{0.98} O	3.244(2)	5.191(6)
Cu _{0.05} Zn _{0.95} O	3.249(6)	5.202(8)
Co _{0.02} Zn _{0.98} O	3.250(4)	5.205(9)
Mn _{0.05} Zn _{0.95} O	3.250(4)	5.205(7)
(Co _{0.01} Mn _{0.01})Zn _{0.98} O	3.251(2)	5.205(9)
(Ni _{0.01} Mn _{0.01})Zn _{0.98} O	3.252(6)	5.207(1)
(Co _{0.01} Ni _{0.01})Zn _{0.98} O	3.250(8)	5.205(5)

detected in some XRD patterns suggesting that the nominal amount of nickel is not completely incorporated into zincite network, remaining as free NiO, in accordance with a previous report [15].

The calculated unit cell parameters are shown in Table 3 for some representative pigments of the families M_xZn_{1-x}O and (MM')_xZn_{1-x}O with M/M' = Mn, Co, Ni, Cu; and x below 0.02. As can be seen from this table all the cell parameters are very similar to ZnO-zincite and some trends could be found within doping. The variation of a and c parameters follow the order Ni²⁺ (0.55 Å) < Cu (0.57 Å) < Co (0.58 Å) ≈ Mn (0.66 Å) which approximately correlates the increase of the cationic size. This suggests that in M_xZn_{1-x}O oxides there is a fair correlation between the crystal radii of dopants and the cell dimensions.

On the other hand, in the case of Ni²⁺ phase due to its smaller size in comparison with Zn²⁺ (0.60 Å) the cell parameters tend to decrease slightly due to substitution. Moreover in Mn-containing oxides an increase towards higher values of unit cell dimensions is attributed to the Mn²⁺ size being greater than Zn²⁺. However it is more difficult to explain why in Cu(II) and Co(II) materials containing smaller crystal ionic radii dopants the lattice parameters of the substituted oxides are higher than those of ZnO.

In conclusion XRD characterization gives support to the evidence of incorporation of M(II) doping cations in the bivalent

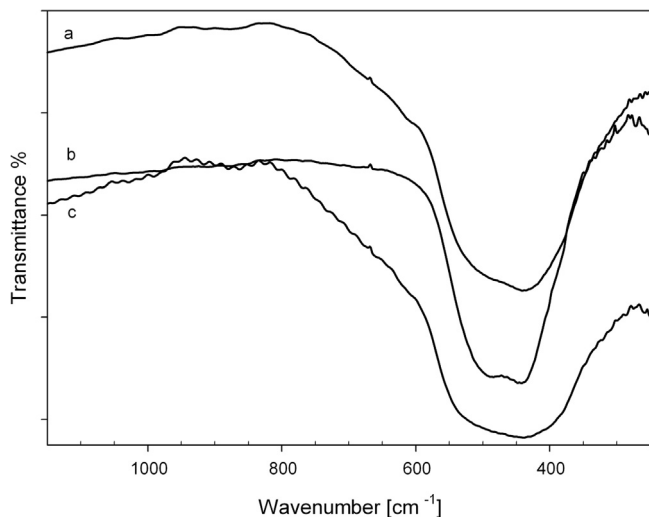


Fig. 2. FTIR spectra of pigments: (a) $\text{Mn}_{0.05}\text{Zn}_{0.95}\text{O}$, (b) $(\text{Mn}_{0.15}\text{Ni}_{0.05})\text{Zn}_{0.8}\text{O}$, and (c) $(\text{Mn}_{0.01}\text{Co}_{0.01})\text{Zn}_{0.98}\text{O}$.

state in zincite lattice forming a solid solution. The shift of crystal parameters due to the M(II) isomorphous substitution is in agreement with previous papers [15,17].

The FTIR spectra of the materials were recorded in order to complete the structural characterization. Some representative infrared spectra are shown in Fig. 2. As can be seen the only signal detected at 440 cm^{-1} is assigned to Zn–O antisymmetric stretching vibration of the ZnO_4 units forming the zincite structure [12,14,18]. No additional bands or significant displacements in wavenumbers are observed suggesting that M(II) chromophore cations occupy the same crystal site with their vibrations coupled with those of ZnO. Due to the vibrational coupling MO_4 and ZnO_4 are undistinguishable. This spectroscopic behaviour gives additional support to XRD analysis regarding the formation of solid solutions $\text{M}_x\text{Zn}_{1-x}\text{O}$ or $(\text{MM}')_x\text{Zn}_{1-x}\text{O}$ by incorporation of M(II) in the tetrahedral crystal site of Zn(II) in zincite (ZnO) structure.

3.2. Study of the enamels

The pigments were submitted to test by enamelling with a transparent glaze free of ZnO. This type of frit was provided by a local industry which manufactures roof and floor tiles and it is representative of a single firing procedures currently applied in the plant. The approximate composition, expressed in equivalent oxide wt% is presented in Table 2. The distinctive feature of a transparent frit is the high SiO_2 content and simultaneously the absence of ZnO which is usually present in opaque glazes. Furthermore a significant amount of boron as flux and glass former is present in the composition of the glaze. In addition a high softening point is expected and confidently these materials could be used in single firing schedules due to the possibility to complete the ceramic biscuits reactions during the enamelling process.

IR spectroscopy was applied to characterize the vitreous components present in each frit, prior to the preparation of the corresponding enamels. As can be seen in Fig. 3, the strongest

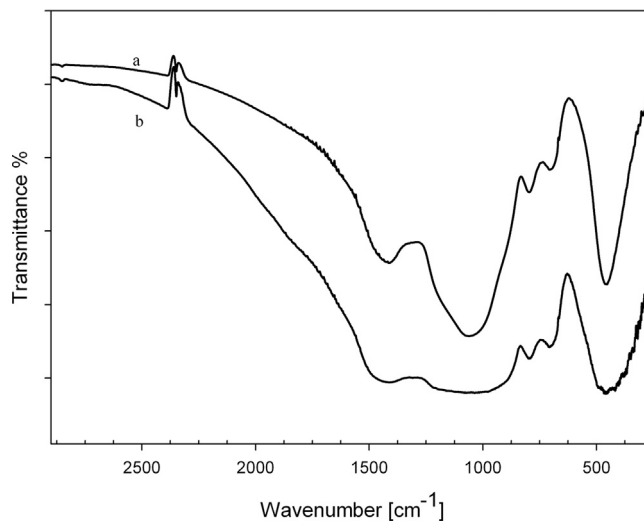


Fig. 3. FTIR spectra of (a) transparent frit and (b) enamels.

band centred in the $1070\text{--}1010\text{ cm}^{-1}$ range can be assigned to Si–O antisymmetric stretching, and the medium intensity band observed around $475\text{--}400\text{ cm}^{-1}$ belongs to OSiO bending vibration modes, as in disordered SiO_4^{4-} tetrahedral groups present in amorphous SiO_2 and three-dimensional silicates [18]. In addition the band in the high energy region, located at 1400 cm^{-1} , and the medium intensity absorption located around 700 cm^{-1} are attributed to the borate units in these glasses. The strong band at 1400 cm^{-1} is a distinguishable feature of the chain anions of the type $(\text{BO}_2)_n^{n-}$, as in sodium metaborate and magnesium pyroborate [19]. Moreover when each glass is thermally treated within the range $850\text{--}1000\text{ }^\circ\text{C}$, the same spectral pattern is obtained, suggesting that the structural arrangement and composition in these materials are maintained during firing and after cooling, in absence of pigment.

The XRD diagrams of enamels fired during the thermal cycle were recorded. The patterns can be seen in Fig. 4 for a representative sample. Some diffraction peaks, belonging to the pigment and the principal peaks of willemite, are observed over the broad “dome” located at around $2\theta=27^\circ$ and 23° from the glass.

In order to explore the interaction between pigment and frit, the enamels were formed by using 10% of one of the pigments, in the thermal range $25\text{--}1000\text{ }^\circ\text{C}$, holding each temperature during 1 h and then slowly cooling at around $2.5^\circ/\text{min}$. The batches were investigated, in detail, by XRD. The XRD patterns of enamels obtained at a relevant thermal interval are shown in Fig. 4a–c. As can be seen the formation of willemite is detected at $750\text{ }^\circ\text{C}$, its presence in coexistence with the pigment is observable at $800\text{ }^\circ\text{C}$, and the subsequent growth of willemite phase upon heating up to around $850\text{ }^\circ\text{C}$, at the expense of pigment reaction with frit, which could be ascertained because only willemite peaks were detected while pigment peaks have almost disappeared at this temperature. Upon heating up to $1000\text{ }^\circ\text{C}$ these diffraction lines disappeared suggesting that the particles lose their crystallinity by dispersion in the glassy boron–silicate matrix.

Based on XRD data, the coloured coating obtained is attributed mainly to the formation of crystalline M(II) doped- Zn_2SiO_4 within

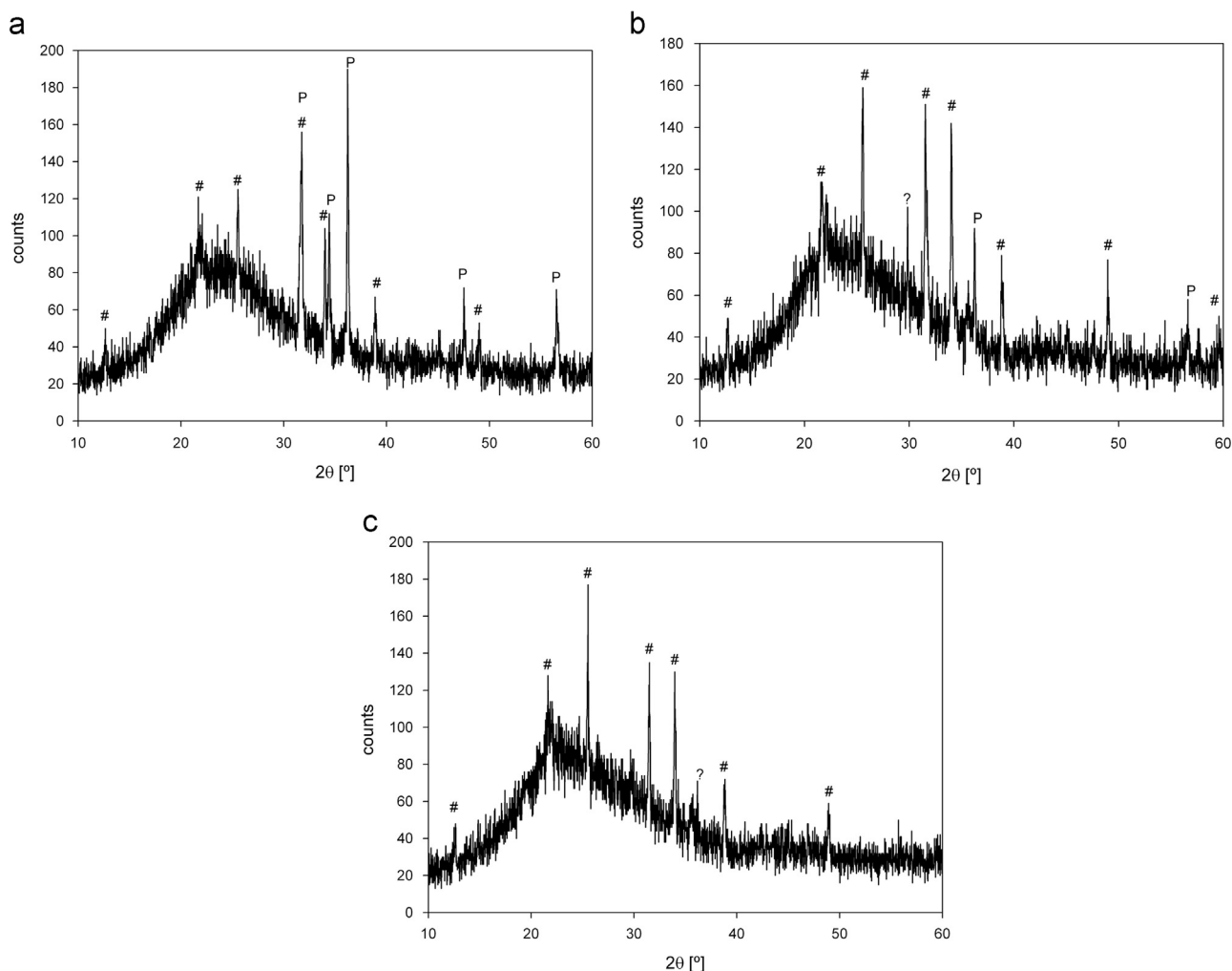


Fig. 4. XRD pattern of the enamel containing $(\text{Mn}_{0.025}\text{Co}_{0.025})\text{Zn}_{0.95}\text{O}$, obtained at: (a) 750 °C, (b) 800 °C and (c) 850 °C. The principal lines of willemitte (#) and pigment (P) are marked.

the glassy matrix. This solid state reaction is mediated by the diffusion of chromophore M(II) and Zn cations from the pigment into the silicate lattice, entering into the Zn(II) site of willemitte by maintenance of the tetrahedral coordination.

A colours virage during this heating interval can be observed while forming the enamels. Consequently, the colouration is developed due to the formation of M(II)-doped willemitte as a result of the pigment–frit interaction, during firing.

According to the FTIR study of the enamels, the main general features of the spectra are maintained during the enamelling process, as can be seen in Fig. 3. These evidences suggest that the boron–silicon glassy networks accommodate zinc and M(II) cations while remain unchanged during the colour formation.

To confirm the dispersion of the coloured phase in the glaze, the SEM micrographs were taken. As can be seen in Fig. 5, the SEM image depicts a homogeneous microstructure lacking surface defects, as cracks or non-homogeneities. In addition the EDAX scanning of the sample was registered confirming that the global elemental composition of the

enamels is consistent with the chemical composition of the pigment–frit batch analysed. Consequently the microscopy data suggest that the pigments are incorporated into the amorphous matrix and the composition is homogenised during firing at 1000 °C. In this way it was observed that the pigments are well dispersed in the glassy matrix, in accordance with diffractometric and spectroscopic evidences.

3.3. Colorimetric characterization of enamels

The colorimetric measurements were performed on white ceramic biscuits enamelled by adding 5% pigment to a transparent boron–silicate glass free of ZnO, of the type used for ceramic tiles and sanitary wares, in a single firing process.

The resulting colorimetric values of all the specimens are detailed in Tables 4–6. The CIELab parameters of the doped-zincite pigments are not maintained when the enamelling procedure occurs because the M(II) chromophores incorporated in the vitreous frit generate willemitte by pigment–frit interaction, as already discussed. In this way, novel palettes of colours appear in the chemical rearrangement.

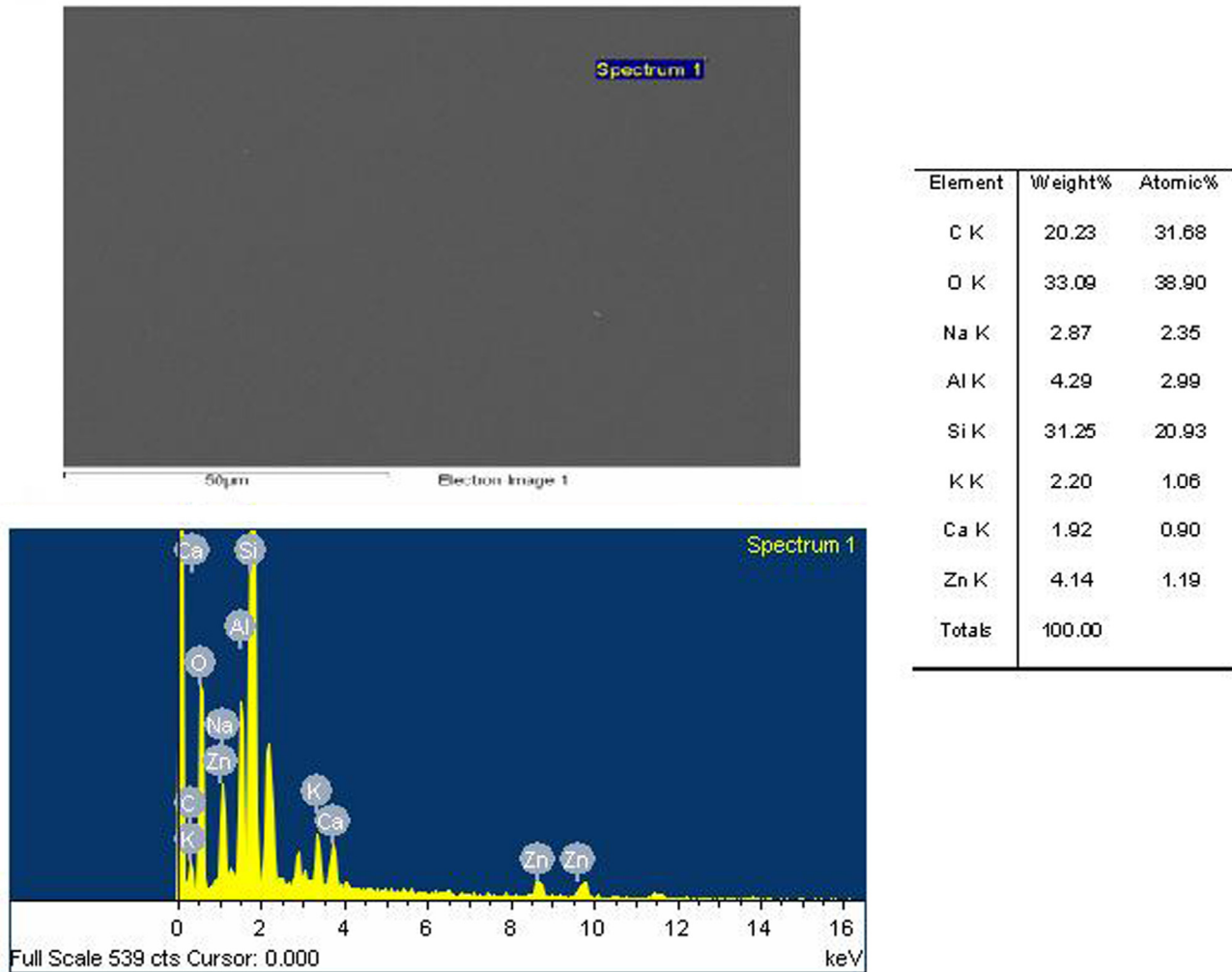


Fig. 5. SEM micrograph and element composition of $(\text{Mn}_{0.015} \text{Ni}_{0.015})\text{Zn}_{0.97}\text{O}$ -transparent frit-enamel.

The colours virage of M(II)-bearing pigments are from deep green to deep blue for Co-, from light green to turquoise for Cu- and from different yellowish hues to pale yellow or brown coatings in the case of Mn- and Ni-, respectively.

In the case of the materials $(\text{MM}')_x\text{Zn}_{1-x}\text{O}$, the simultaneous doping of two bivalent cations results in a wide palette of green, yellow, and brown shades which virage by glazing towards various shades of hues.

3.3.1. Enamels containing $\text{Co}_x\text{Zn}_{1-x}\text{O}$

Regarding the enamels containing $\text{Co}_x\text{Zn}_{1-x}\text{O}$ solid solution, originally green, the incorporation to various vitreous commercial frits, performed in the 800–1000 °C range, give rise to deep blue colouration due to the in-situ formation of Co-doped Zn_2SiO_4 -willemite [14]. The deeper blue colouration is attributed to the presence of Co(II) chromophore in a more distorted tetrahedral site in the vitreous matrix. Therefore Co-doped willemite is better suited for ceramic application because the colouring performance is enhanced in comparison with the other commonly typically used blue colourants such

as spinel CoAl_2O_4 or olivine Co_2SiO_4 [4]. The in-situ formation is facilitated by the reaction between $\text{Co}_x\text{Zn}_{1-x}\text{O}$ pigment and SiO_2 from the frit due to the maintenance of tetrahedral Co and Zn crystal symmetry sites during enamelling [14]. This is an advantageous strategy which contributes to enhance the thermal stability of the colour in the glaze.

3.3.2. Enamels containing $\text{Cu}_x\text{Zn}_{1-x}\text{O}$

The behaviour of Cu-doped zincite pigments in the transparent ceramic glaze was analysed. The effect of the degree of substitution in the $\text{Cu}_x\text{Zn}_{1-x}\text{O}$ pigments with x up to 0.2, on the colour parameters, was analysed as can be seen in Table 4. The CIELab values gradually increase by doping, implying the progressive colour change with gain of both colour saturation (decreasing L) and chroma (decreasing $-a$ and b). In addition according to Fig. 6 the sharp decrease of $-a$ values indicates the more green the colour hue and simultaneously less yellow due to the decrease of b value.

All the compositions are located in the green and blue-green regions of the CIELab chromatic diagram, in the domain of Cr

Table 4
Colorimetric parameters of enamels containing Cu(II)–ZnO pigments.

Glazes containing Cu(II)–ZnO pigments	<i>L</i>	<i>a</i>	<i>b</i>
Cu _{0.01} Zn _{0.99} O	82.52	−2.91	11.90
Cu _{0.05} Zn _{0.95} O	76.26	−11.47	6.98
Cu _{0.1} Zn _{0.9} O	71.44	−14.41	3.15
Cu _{0.2} Zn _{0.8} O	62.15	−19.15	1.88
(Cu _{0.01} Co _{0.01})Zn _{0.98} O	82.01	3.02	22.00
(Cu _{0.01} Mn _{0.01})Zn _{0.98} O	83.68	−0.73	12.63
(Cu _{0.01} Ni _{0.01})Zn _{0.98} O	83.00	−3.05	12.10

Table 5
CIE*Lab* parameters of (MnM')_xZn_{1−x}O based enamels.

(MnM') _x Zn _{1−x} O based enamels	<i>L</i>	<i>a</i>	<i>b</i>
(Mn _{0.01} Cu _{0.01})Zn _{0.98} O	83.68	−0.73	12.63
(Mn _{0.01} Co _{0.01})Zn _{0.98} O	73.10	1.31	0.70
(Mn _{0.025} Co _{0.025})Zn _{0.95} O	54.03	2.54	−18.35
(Mn _{0.01} Ni _{0.01})Zn _{0.98} O	82.17	3.50	19.16
(Mn _{0.015} Ni _{0.015})Zn _{0.97} O	72.69	4.82	20.31
(Mn _{0.025} Ni _{0.025})Zn _{0.95} O	74.33	7.76	22.52
(Mn _{0.15} Ni _{0.05})Zn _{0.8} O	68.73	10.11	29.99

Table 6
CIE*Lab* parameters of (NiCo)_xZn_{1−x}O based enamels.

(NiCo) _x Zn _{1−x} O based enamels	<i>L</i>	<i>a</i>	<i>b</i>
(Ni _{0.01} Co _{0.01})Zn _{0.98} O	71.44	1.59	5.48
(Ni _{0.015} Co _{0.015})Zn _{0.97} O	56.99	1.02	1.22
(Ni _{0.025} Co _{0.025})Zn _{0.95} O	56.58	1.06	1.00

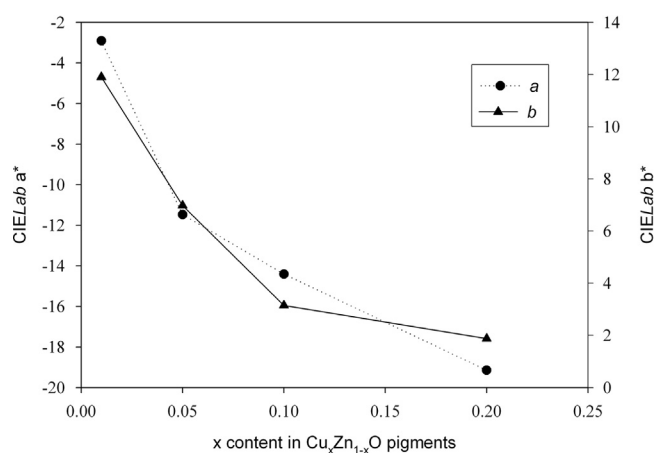


Fig. 6. Chromatic change dependence with *x* in the Cu_{*x*}Zn_{1−*x*}O containing glazes.

(III) pigments as Cr₂O₃. Moreover the highly substituted Cu_{0.2}Zn_{0.8}O phase is very close to the region typical of glazes elaborated with turquoise spinel CoCr₂O₄ commercial pigments with *−a* and *b* values lying around *−20* and *−5*, respectively.

Finally the use of this family of Cu_{*x*}Zn_{1−*x*}O pigments to achieve green and blue-green hues is advantageous because these materials are ecologically friendly substitutes of chromium oxides or mixed oxides. Nevertheless the colour intensity of the enamels, measured by *L* values which increases with Cu-doping, is rather low in comparison with the mentioned Cr(III) pigments and therefore larger concentrations should be necessary.

3.3.3. Glazes based on bimetallic substituted pigments (MM')_xZn_{1−x}O

3.3.3.1. (Cu_{0.01}M'_{0.01})Zn_{0.98}O, with M' = Mn, Co, Ni, series. The colorimetric parameters of the family of pigments (Cu_{0.01}M'_{0.01})Zn_{0.98}O, with M' = Mn, Co, Ni, are also displayed in Table 4. As can be seen due to the low degree of substitution the value of the coordinate *L* is high, characteristic of materials with light colouration. As can be observed, except for the Co-bearing material, the chromatic *a* and *b* values are close to those of the reference Cu-doped pigment, with low substitution Cu_{0.01}Zn_{0.99}O, suggesting that the presence of Cu in the chromatic combination MM', is responsible for the colour hue in the palette of green hues. Particularly in the case of the pair CuNi almost the same light green tonality is achieved in the glazed samples.

However in the case of the simultaneous substitution of Zn by the CuCo pair a yellowish tonality is generated, with chroma characterized by small *+a* and large *+b*. These values are close to those of the reference ceramic pigments of the type zirconia vanadium yellow, commonly used when a moderate pure yellow shade is required [7].

3.3.3.2. (MnM')_xZn_{1−x}O, with M' = Co, Ni, Cu. A large series of (MnM')_xZn_{1−x}O materials was investigated. The obtained glazes show a wide palette ranging from green when M' is Cu, as already described; bluish grey if M' is Co and shades of light yellow/brown in the case that M' is Ni. The colorimetric behaviour of doped-zincite pigments containing the combination of Mn with other M' colour cations and variable degree of substitution was analysed. As detailed in Table 5, the CIE*Lab* values of the samples dominate the region of yellow and brown glazes, characterized by *+a*/*+b* chromatic values.

The plots depicted in Fig. 7 show the dependence of the CIE*Lab* parameters of enamels containing equally substituted Mn/Ni formulations (MnNi)_xZn_{1−x}O, for *x* = 0.01, 0.015, 0.025, from the dopant content. According to the figure both *a* and *b* parameters increase gradually showing an almost linear trend with increasing substitution. This colorimetric behaviour gives rise to a light yellowish-brown shade fairly pure which is governed by *+b* values *~20* and low values of *+a*. Furthermore the colour intensity darkens since the coordinate *L* decreases while *x* increases.

In the case of the glazes containing the combination MnNi with a higher amount of Mn, such as (Mn_{0.15}Ni_{0.05})Zn_{0.8}O, according to the data in Table 5, a shift towards brown shade is produced since the *a* parameter reaches the value *+10* and simultaneously the value of the parameter *+b* grows towards yellow hues. Consequently this material generates hues which are intermediate between V–Zr yellow and CrFeZnAl brown ceramic pigments. If the same material is prepared without

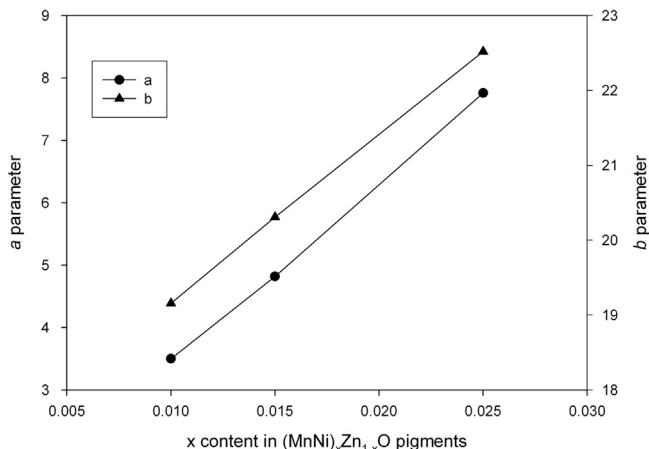


Fig. 7. CIELab parameters relationship with (MnNi) content in enamels.

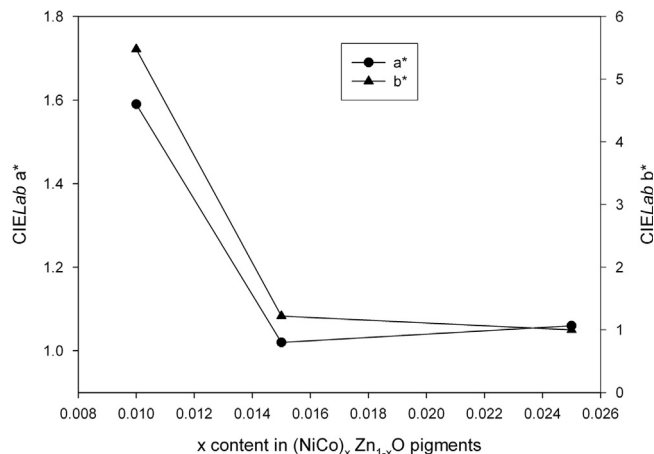


Fig. 8. CIELab parameters relationship with (NiCo) content in enamels.

intermediate grindings the yellow shade of the enamel darkens. In this way the value $+a$ grows more than $+b$ getting close to the typical set of coordinates of brown hues in the small region near $+a = +b = 10$. This brown tonality could be attributed to the presence of the mixed oxide Mn_3O_4 -hausmanite, as detected by FTIR spectroscopy. The colorimetric measurements suggest that the mixed valence of Mn is maintained during enamelling contributing to darkening of the colour due to low lightness achieved.

In the case of the glazes containing the pigment with lower amount of Mn, $(Mn_{0.05}Ni_{0.15})Zn_{0.8}O$, a shift towards yellow shade is produced and simultaneously the colour lightens reaching Lab values close to those of the so called “VZr yellow”. In fact the value of chroma $+b$ grows more markedly than $+a$ and is the highest in the series of MnM' pigments. This material was also tested in a *porcellanato* admixture thermally treated at $1200\text{ }^\circ\text{C}$ and a similar hue was obtained.

On the other hand, the enamels prepared with MnCo pigments new shades of “Co blue” tending to purple hues are obtained. In the case of the less substituted $(Mn_{0.01}Co_{0.01})Zn_{0.98}O$ the colour is pale with $+a$ and $+b$ parameters close to the centre of coordinates 0,0. However if the amount of Co increases as in the pigment $(Mn_{0.025}Co_{0.025})Zn_{0.95}O$, a deeper chroma is obtained in the glaze with a sharp decrease of the parameter $-b$ indicator of blue. This behaviour is typical of Co(II) chromophore. Indeed in this glaze the colorimetric parameters are close to those measured for the enamels containing the pigment $Co_{0.02}Zn_{0.98}O$, in a vitreous aluminosilicate matrix, reported in a previous paper [14]. A blue coloured porcelainized specimen was achieved using this pigment in the batch calcined at $1200\text{ }^\circ\text{C}$.

Finally in the series of Mn(II) containing pigments, the chromatic behaviour is mainly governed by the $M'(II)$ accompanying cation. The role of Mn in the glazes seems to be a modifier of the typical chroma attributed to $M'(II)$: Co, Ni or Cu, contributing to enhance the chromatic palette.

3.3.3.3. $(NiCo)_xZn_{1-x}O$. In the case of the glazes prepared using NiCo–zincite pigments the glassy coatings give rise to a palette of greyish blue. According to the colorimetric values

detailed in Table 6 the presence of Co(II) seems to be determinant for the blue chroma and the other $M'(II)$ cation contributes to modify the palette of blue shades.

As can be seen in Fig. 8 a sharp decrease of both a and b parameters is noticeable, more markedly in the case of b , if the concentration of chromophore cations is below $x=0.015$. For a higher degree of substitution both chromatic parameters keep almost constant. The incorporation of the pigment $(Ni_{0.025}Co_{0.025})Zn_{0.95}O$ to *porcellanato* generates at $1200\text{ }^\circ\text{C}$ a similar greyish blue colouration.

3.4. Electron spectroscopy characterization of enamels

The optical absorption spectra of the cobalt containing enamels: $(Mn_{0.025}Co_{0.025})Zn_{0.95}O$ and $(Ni_{0.025}Co_{0.025})Zn_{0.95}O$, measured by reflectance, were obtained in order to interpret the formation of colour. As can be seen in Fig. 9 a broad split band covers almost the entire visible region. This absorption band lying in the range 500–700 nm is well separated from the adsorption edge. The composing peaks, marked at around 520, 600 and 640 nm, are assigned to the crystal field electronic transitions in high spin Co^{+2} (d^7), in tetrahedral distorted coordination [9,15,20]. In addition this spectral pattern resembles the optical spectra of Co-bearing willemite pigments, available in the literature [21]. These observations clearly confirm that cobalt is in bivalent oxidation state, occupying Zn(II) site, which is responsible for the intense blue hues observed in the glazes, in accordance with previous report [14]. However some different features are observed in the low energy region near the edge of the visible spectrum which are attributed to the presence of the chromophore $M(II)' = Mn, Ni$ accompanying doping cations. According to available data Ni(II)-doped ZnO presents a low absorption peak, overlapped with the adsorption edge of zincite, which decays at 500 nm and in the case of Mn(II) it absorbs more strongly up to 600 nm [15,20]. In consequence the visible light below 500 nm, belonging to blue, is mostly transmitted by the glazes, more markedly in the case of $(Mn_{0.025}Co_{0.025})Zn_{0.95}O$, in consistence with the deeper blue chrome measured in this glaze.

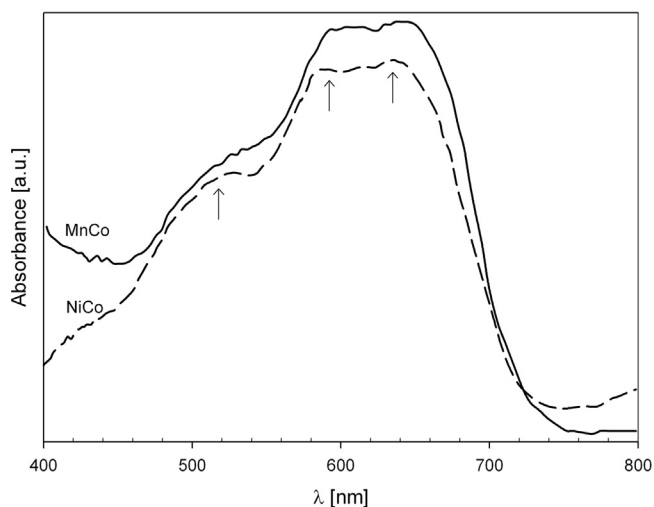


Fig. 9. DRS of $(\text{Mn}_{0.025}\text{Co}_{0.025})\text{Zn}_{0.95}\text{O}$ (MnCo) and $(\text{Ni}_{0.025}\text{Co}_{0.025})\text{Zn}_{0.95}\text{O}$ (NiCo) pigments in the glazes.

4. Conclusions

A family of coloured $\text{M}_x\text{Zn}_{1-x}\text{O}$ and $(\text{MM}')_x\text{Zn}_{1-x}\text{O}$ doped-zincite oxides with $(\text{M}/\text{M}' = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu})$ and x not higher than 0.2 was synthesized and characterized by XRD analysis and FTIR spectroscopy. When Mn, Co, Ni and Cu are present in the Zn(II) site, light brown, deep blue, pale yellow and green, are achieved respectively. Furthermore the simultaneous doping with a combination MM' results in various shades of colours.

The performance of these doped-zincite pigments enamelled in a transparent frit, obtained at 1000°C , was evaluated. According to XRD characterization M(II)-doped willemite phase is formed at around 700°C due to the pigment–frit interaction. Simultaneously a virage of the original colour of the pigments is observed. Upon heating at 1000°C the particles lose their crystallinity by dispersion in the glassy matrix. The homogeneity of the coating was confirmed by SEM–EDX measurements.

Some of the materials were also successfully tested for their ability to colour *porcellanato* tiles processed at 1200°C .

The colorimetric characterization of the enamels was carried out by CIELab data.

The colours virage of enamels formed with M(II)-bearing pigments are from deep green to deep blue for Co-, from light green to turquoise for Cu- and from different yellowish hues to pale yellow or brown coatings in the case of Mn- and Ni-, respectively. In the case of the materials containing $(\text{MM}')_x\text{Zn}_{1-x}\text{O}$ pigments, the simultaneous doping of two bivalent cations results in a wide palette of green, yellow, and brown shades which virage by glazing towards various new shades, enlarging the palette.

The in-situ colouring strategy seems to be advantageous in order to maintain the stability of the palette of colours. Due to the intense colouration and thermal stability of the colours during glazing a small amount of pigment is necessary and consequently a minimisation of transition metal chromophores is possible.

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