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Interaction of Co–ZnO pigments with ceramic frits: A combined study by XRD, FTIR and UV–visible

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Abstract

The development of blue colour when mixed oxides of the system $Co_xZn_{1-x}O$ are incorporated, to industrial frits is reported. The Co–ZnO pigments were prepared by solid state reaction. A complete series of Co(II) substituting Zn(II) in wurtzite lattice was studied, from the structural point of view, by XRD and FTIR. In order to test these materials as ceramic pigments, 5 and 10 wt% compositions of them were enamelled with three different transparent glazes, representative of single and double firing industrial procedures, and then submitted to thermal treatment between 750 and 1000 °C. The frits, of known composition, were fully characterized by FTIR spectra, prior to the mixing with pigments. The change of colour in the glazes was interpreted by analyzing the dependence of the UV–visible electronic spectra (reflectance) of the samples on the heating temperatures. The phases developed in each stage of the thermal treatment as a result of pigment–frit interaction were controlled by XRD data, complemented by vibrational FTIR analysis. The blue colour obtained, once the glazes were formed is attributed mainly to the formation of crystalline Zn_2SiO_4 with Co(II) ions in tetrahedral coordination which remain dissolved, over 1000 °C in the glassy matrix. The colorimetric parameters measured are in good agreement with the structural and spectroscopic analysis. Their values are within the range of typical silicate and aluminate Co(II) pigments. This study demonstrates that ZnO of the pigment is capable of forming its own Zn-based crystals in conventional ceramic frits giving rise to deep blue cobalt glazes.

Keywords: $Co_xZn_{1-x}O$; Co-ceramics glazes; XRD Phase development; IR spectra

1. Introduction

ZnO has been worldly used as white inorganic pigment and cobalt is known to produce various colours when doped in oxide matrices. This transition element is an efficient colouring agent in glasses and ceramic pigments because of the mobility of its 3d electrons. In this way, the green coloured oxides of CoO–ZnO system, with low Co content, have demonstrated to be comparable in their physico-chemical properties with Cr(III) green pigments [1]. Therefore, the Co–ZnO oxides are of interest as new ecological friendly coloured pigments because they can be used as substitutes of chromium oxides.

On the other hand, in recent years oxide solid solutions of Co-doped ZnO have been of great interest for device applications, as in optoelectronics and thermoelectronics, due to their electronic and magnetic properties [2,3].

The experimental work carried out in our laboratory demonstrates that when the green powders of Co–ZnO are incorporated to three kinds of commercial frits, commonly used in the ceramic industry, deep blue glazes are obtained after heating at high temperatures. The blue colour is normally assigned to the incorporation of Co(II) in tetrahedral symmetry of some host lattices as it has been observed in silicate network, in olivine and willemite, or in spinel structures [4].

All the blue ceramic pigments currently known contain Co to some extent when pigment–frit batches are calcined: for instance the substitution of Co(II) at zinc crystal site of the $ZnAl_2O_4$ currently called gahnite and of the silicate $ZnSiO_4$ [4,5] called willemite. Willemite structure is usually preferred for environmental issues because a bluer ceramic pigment is obtained using a lower optimized Co(II) concentration. In the case of porcelainzed bodies the most intense and bright blue color is produced by $CoAl_2O_4$ [6].

In the present study, the change of phases and structural effects caused by the interaction between $Co_xZn_{1-x}O$ pigments

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Table 1
Nominal composition and unit cell parameters of the investigated pigments

Pigments	a [Å]	c [Å]
ZnO	3.246(9) *3.2495*[a]	5.201(7) *5.2054*[a]
$Zn_{0.98}Co_{0.02}O$	3.250(4)	5.205(9)
$Zn_{0.90}Co_{0.10}O$	3.241(0)	5.183(3)
$Zn_{0.75}Co_{0.25}O$	3.247(9)	5.191(4)

[a] Reported values [1].

and industrial frits at different temperatures have been analyzed by XRD and FTIR. The firing behaviour of different composition glazes was evaluated by using variable amount of pigment, within a range of doping Co(II) concentrations. The family of oxides of nominal composition $Co_xZn_{1-x}O$, with $x = 0.02$, 0.10, 0.25 was synthesized and a series of batches containing 5 and 10% pigment mixed with three different ceramic frits were prepared with the aim to produce nuclei for the development of zinc based crystal in the glazes. The color properties of the enamels were analyzed by UV–visible, and CIE*Lab* parameters were determined. Accordingly, the colour development was analyzed by the study of the structural and electronic properties of Co(II) in glassy matrices.

2. Experimental details

The $Co_xZn_{1-x}O$ pigments were prepared using the traditional ceramic procedure. ZnO (Merck, 99%) and $CoCO_3$ (Aldrich) 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 porcelain crucibles in a muffle electrical furnace for 2 h. 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 and monochromatic Cu Kα radiation. 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 minimum squared procedure and refined with a locally modified version of the Werner PIRUM programme.

In an attempt to obtain more information on the interaction between the pigment and ceramic frits, test specimens were prepared by mixing these materials thoroughly. The composition of the frits employed is detailed in Table 2.

Table 2
Approximate composition of ceramic frits (in oxides, wt%)

Oxides (Wt%)	Frit A	Frit B	Frit C
Na_2O	2–3	2–4	4–7
K_2O	1–3	0.5–1	1–3
CaO	3–5	9–12	3–5
PbO	28–32	–	–
ZnO	–	1–4	–
B_2O_3	4–6	15–18	14–17
Al_2O_3	4–6	5–8	9–11
SiO_2	48–50	44–47	60–65
ZrO_2	–	10–15	–

Table 3
Nomenclature of prepared pigment–frit batches, treated at the stated temperatures

Sample	Pigment	Wt% pigment	Frit	T_{max} [°C]
A1	$Zn_{0.75}Co_{0.25}O$	10	FA	800
B1	$Zn_{0.75}Co_{0.25}O$	10	FB	800
C1	$Zn_{0.75}Co_{0.25}O$	10	FC	800
C2	$Zn_{0.98}Co_{0.02}O$	5	FC	750
C2	$Zn_{0.98}Co_{0.02}O$	5	FC	800
C2	$Zn_{0.98}Co_{0.02}O$	5	FC	850
C2	$Zn_{0.98}Co_{0.02}O$	5	FC	900
C2	$Zn_{0.98}Co_{0.02}O$	5	FC	950
C2	$Zn_{0.98}Co_{0.02}O$	5	FC	1000
C3	$Zn_{0.98}Co_{0.02}O$	10	FC	750
C3	$Zn_{0.98}Co_{0.02}O$	10	FC	850
C3	$Zn_{0.98}Co_{0.02}O$	10	FC	950
C4	$Zn_{0.90}Co_{0.10}O$	10	FC	750
C4	$Zn_{0.90}Co_{0.10}O$	10	FC	850
C4	$Zn_{0.90}Co_{0.10}O$	10	FC	950

The mixtures of frits and pigment (5 and 10 wt%) were homogenized in an agate mortar and were wetted at 0.06 kg H_2O/kg dry solid. Cylindrical test specimens were formed with these powders by pressing at 416 MPa. The resulting materials were put onto ceramic biscuits and fired in a muffle electrical furnace. The thermal cycles consisted in heating up to 500 °C at 25 °C/min, keeping this temperature for 1 h and then raising it at 2 °C/min up to different maximum temperatures and maintaining this temperature for another hour. The references of the samples prepared are shown in Table 3.

All the specimens were finally milled and characterized by XRD and FTIR.

Individual samples of each of the pure frits were fired also at different temperatures for comparative purposes.

UV–visible spectroscopy measurements were obtained, by diffuse reflectance, with a Shimatzu UV-300 instrument model, using MgO as a standard. CIE $L^*a^*b^*$ colour coordinates were obtained on glazed tiles containing 10% pigment of different chemical composition with frit C, with a Braive Super Chroma 20 mm colorimeter and a white standard as reference.

3. Results

3.1. Materials

3.1.1. XRD and FTIR structural characterization of Co–ZnO pigments

Samples with increasing content of Co(II) were investigated by X-ray diffraction analysis for compounds of nominal composition $Co_xZn_{1-x}O$. The patterns only show diffraction peaks belonging to wurtzite (W) structure as observed in pure ZnO. This indicates that Co(II) is incorporated into de Zn(II) crystal site in W lattice forming a solid solution without any change of wurtzite lattice. Nevertheless, in the case of the sample with the highest Co content, additional lines assigned to free CoO with rock salt structure were detected in the pattern due to the solubility limit of 20%, under equilibrium conditions in the CoO–ZnO system [7].

The whole pattern could be indexed, based on the hexagonal W structural type. The lattice constants obtained from our refinement can be seen from Table 1. The calculated values are in complete agreement with those previously reported [1]. The incorporation of Co(II) is expected to have slight effect on the lattice parameters of ZnO since the ionic radii for four coordinated Co^{+2} (0.72 Å) in high spin d^7 electronic configuration is only slightly smaller than for Zn^{+2} (0.74 Å) with d^{10}.

An analysis of the dependence of the lattice parameters of Co-substituted phases from the doping content shows that all the calculated values, for both a and c cell parameters, are closer to the parameters measured for pure ZnO (as a reference) and also that most of them are slightly smaller than the reported for pure ZnO [1]. It is possible that as a result of thermal treatment during incorporation of rock salt CoO at high temperatures, O-defects (vacancies or the presence of Co^{+3}) are created in the host ZnO lattice.

Once the materials were fully analyzed by XRD the vibrational study was carried out. The IR spectra recorded for all the investigated materials are identical. The spectra depicted in Fig. 1 clearly shows one strong broad band centered at 440 cm^{-1} assigned to antisymmetric stretching mode of the tetrahedral ZnO_4 group present in the wurtzite–ZnO structure. No additional bands or displacements in wavenumber are observed, confirming the results obtained by XRD measurements of solid solution $Co_xZn_{1-x}O$ by incorporation of Co(II) in the same tetrahedral site of Zn(II) in ZnO structure.

3.1.2. *Characterization of frits*

Co–ZnO pigment samples were submitted to test by enamelling with three different transparent glazes. These frits were provided by a local industry which manufactures roof and floor tiles. The glazes were selected to be representative of the double and single firing procedures currently applied in the plant.

The approximate compositions, expressed in equivalent oxide weight percentage are presented in Table 2, labelled as A, B and C. In frit A, the main feature is the presence of a high amount of lead. This material should be suitable for traditional double firing at rather low temperature (~800 °C) giving rise to brighter enamels than the rest of the glazes. Meanwhile in the case of frits B and C a significant amount of boron is present as glass former. In the case of B, ZrO_2, as bivalent opacifying, oxide is accompanying SiO_2. This glass is also characterized by a significant amount of CaO and by the fact that it is the only frit containing some ZnO in the formulation. A higher melting point is expected and confidently this material could be used in a single firing processing. Glasses made with frit C have the highest SiO_2 content, consequently, a higher melting point is expected in order to let ceramic biscuits reactions to be accomplished before melting during the single firing schedule.

XRD measurements are not suitable for characterization of frits and glazes since these materials are amorphous. No diffraction peaks are detected; instead, a broad "dome" centered near $2\theta = 27°$, 25° and 23° is observed for A, B and C, respectively, as can be seen in Fig. 2a. Therefore, IR spectroscopy was applied in order to analyze the composition of phases present in each frit prior to the preparation of the corresponding enamels.

The spectral pattern of frit B, which is shown in Fig. 3, is identical to that recorded for frit C. Whereas in the case of frit A the spectrum is rather simpler, as may be seen in the same figure. These differences can be explained having in mind that although SiO_2 is the major glass forming network in the three materials, in frits B and C a similarly high amount of B_2O_3 is also present. The spectral assignment was carried out by comparison with the spectra of borate and silicate glasses already reported [8–13].

In all cases the strongest band centered in the 1070–1010 cm^{-1} range can be assigned to Si–O antisymmetric stretching, whereas the medium intensity absorption band observed around 475–400 cm^{-1} belongs to OSiO bending vibration modes in disordered SiO_4^{4-} tetrahedral groups present in amorphous SiO_2 and three-dimensional silicates [8–10].

The main features allowing differentiation between both types of building units, silicate and borate in these glasses, are

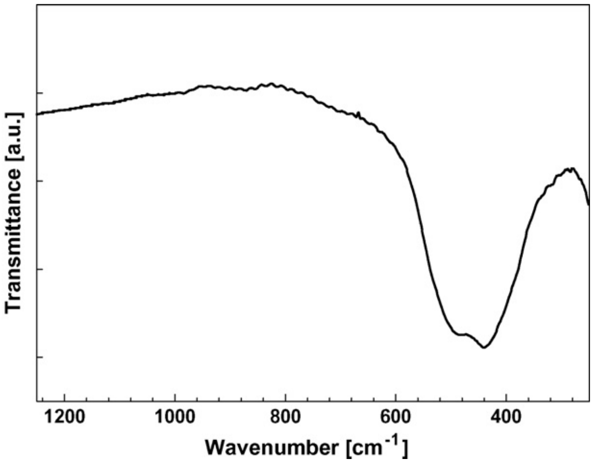

Fig. 1. FTIR spectra of a representative pigment ($Co_{0.10}Zn_{0.90}O$).

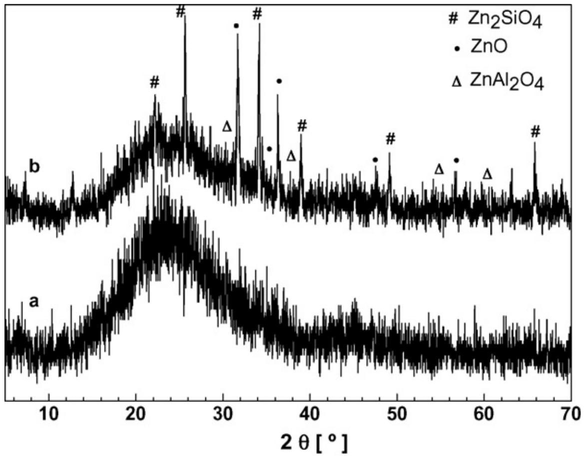

Fig. 2. Comparative XRD patterns of: Frit C (a) and C1glaze sample treated at 800 °C (b).

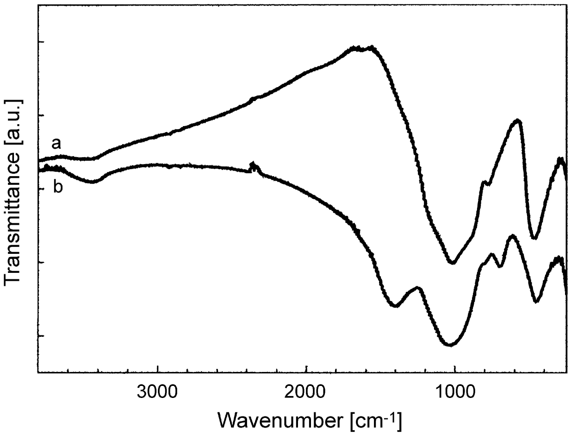

Fig. 3. FTIR spectra of the frits used in the batches detailed in Table 3: Frit A (a) and Frit B (b).

the medium intensity band of higher energy located at 1400 cm^{-1} in B and C materials, and the medium intensity absorption located around 700 cm^{-1}.

The IR spectrum of a borate is a useful tool for its identification since oxoanion structures are known to exist in a variety of condensation degrees going from isolated to complex rings and infinite chains, similar to silicates but with two possible coordinations, triangular and tetrahedral. Complex anions arising from polymerization of basic triangular BO_3^{3-} or tetrahedral BO_4^{4-} units, alone or in combination, may be distinguished by their IR spectra [11–13]. According to the spectra depicted in Fig. 3 for frit B, the strong band at 1400 cm^{-1} is a distinguishable feature of chain anions $(BO_2)_n^{n-}$ similar to the structure of crystalline sodium metaborate and as in Mg-pyroborate [11]. BO_3^{3-} groups are easily identified since they lead to a strong absorption above 1000 cm^{-1}, a strong band in the 700–800 cm^{-1} region and one or two weaker bands below 700 cm^{-1}.

The same spectral pattern is obtained when each glass is thermally treated within the range 725–1000 °C, suggesting that the structural arrangement and composition in these materials are maintained after firing and cooling, in absence of pigment. In the case of frit A, at 800 °C it was clearly softened whereas in the rest of the pellets made out of B and C, rounded borders are observed as evidence of incipient fusion at this temperature, in accordance with the respective compositions.

3.2. Study of the interaction pigment–frit in the thermal range 750–1000 °C

$Co_xZn_{1-x}O$ solid solution cannot be used as original green pigment, in substitution of the so called green Cr, for ceramic applications, since during the thermal treatment, the Co-tetracoordinated incorporated in the vitreous frit generates a characteristic blue coloration called Co blue. Due to this fact the mixtures of enamels of the compositions detailed in Table 3, are initially green and depending on the temperature, kind of frit, quantity of Co(II) in the original pigment and mass of pigment used to prepare the enamel, the pellets turn from green to green-blued, turquoise, blue-greenish and finally deep blue.

3.2.1. Study of the enamels based on $Co_{0.25}Zn_{0.75}O$ obtained, with each one of the frits at 800 °C

In order to carry out a systematic study, a 10 wt% of $Co_{0.25}Zn_{0.75}O$ pigment was added to the three commercial frits: A, B and C. The batches were initially submitted to a thermal treatment up to 800 °C as stated for the first three formulations listed in Table 3.

When these materials are analysed by the XRD, besides the characteristic "dome" of the glassy matrix, some diffraction peaks, attributed to crystalline phases resulting from the interaction between pigment and frit, are observed in the pattern. As a representative example the pattern of sample C1 is shown in Fig. 2b. In this X-ray powder diagram may be distinguished: ZnO from the pigment, Zn_2SiO_4 (JCPDF:37-1485) and $ZnAl_2O_4$ (JCPDF:05-0669). Co(II) is expected to be distributed among these phases substituting Zn(II) in its crystal site. The same result is observed for sample containing frit A. Meanwhile, in the case of frit B, the silicate $CaSiO_3$ (JCPDF:43-1460) diffraction lines accompanying characteristic peaks of the pigment and $ZnAl_2O_4$ were observed.

Based on the relative intensities of the typical lines observed in the patterns, the proportion of phases present in the composite material (enamels) could be estimated as: In frit A, $ZnO > Zn_2SiO_4 > ZnAl_2O_4$; in frit B, $ZnO > Zn_2SiO_4 \cong CaSiO_3 > ZnAl_2O_4$; and in frit C, $ZnO \cong Zn_2SiO_4 > ZnAl_2O_4$. These results suggest that the type and amount of crystalline phases formed during the incorporation of pigment to the different frits are very much alike, despite the difference in chemical composition of the glasses.

The formation of the zinc silicate, Zn_2SiO_4–willemite, is the result of the chemical reaction between SiO_2, major component in the frits, and ZnO, the structural base of the pigment. On the other hand $ZnAl_2O_4$–spinel, clearly detected although in less extent, should be formed by similar interaction between ZnO-pigment and Al_2O_3 supplied by all the frits, according to Table 2. The presence of $CaSiO_3$-wollastonite, detected exclusively in the case of frit B, is attributed to the existence of an appreciable amount of CaO in this glass. On the other hand, this is the only frit which contains a low amount of ZnO prior to the incorporation of Co–ZnO pigment.

The FTIR study of enamels synthesized at 800 °C could be fully interpreted in correlation with the structural information from XRD measurements. The new bands associated to crystalline compound were identified by comparison with pure mineral spectra from a FTIR-library. The main general feature of these spectra is maintained after pigment–frit interaction, suggesting that silicon and boron polyhedra disorder lattice is basically unchanged when the blue colour is developed at this temperature. Nevertheless, the presence of the new crystalline phases upon firing at 800 °C, detected by XRD analysis, also cause subtle changes in the vibrational spectra of all enamels under analysis.

The most noticeable change for the specimen labelled A1, as may be seen in Fig. 4a, is the broadening of the typical

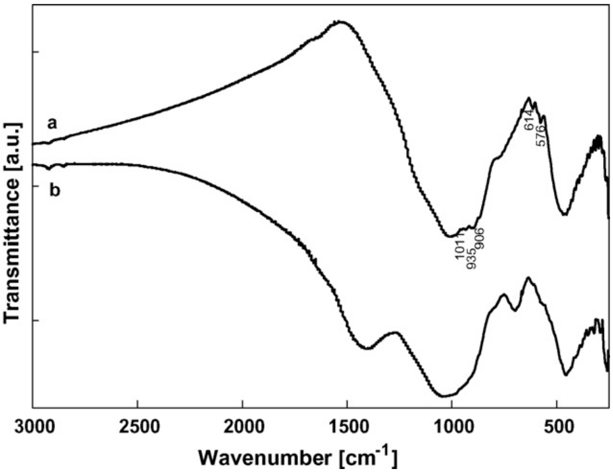

Fig. 4. FTIR spectra of formulations A1 (a) and B1 (b), treated at 800 °C, showing pigment–frit interaction.

stretching absorption of silicate network and the apparition of a multiplet band in 1011,935 and 906 cm^{-1}, due to Zn_2SiO_4, along with the diminution of the weak band of SiO_4^{4-} angular deformation (the doublet located in 784–773 cm^{-1}). These features are also associated to the presence of a new medium intensity splitted band located in 614–576 cm^{-1}, assigned to the same compound, coupled with the stretching of the Al–O bonds belonging to the octahedral AlO_6 present in the $ZnAl_2O_4$–spinel phase, formed in lower proportion, as stated before.

At the same time, the spectral behaviour of the rest of the blue glasses, richer in boron content, which are forming from the other frits B and C, is similar. The most remarkable difference between them is that in the case of formulation B1, a greater broadening without splittings, poorly resolved, appears in the low energy side of the intense band associated to SiO_4, as shown in Fig. 4b. This feature is coincident with the most characteristic band in the spectrum of the mineral $CaSiO_3$ confirming the presence of this compound as a by-product of the frit–pigment reaction, along with the absence of $ZnAl_2O_4$-spinel bands.

The spectral signals of enamels with frit C remain unaltered, during the phase changes, taking place at high temperature. Surely, the features of the silicate bands are maintained due to the highest SiO_2 amorphous content in these materials.

Regarding the medium intensity band located at 1400 cm^{-1} attributed to BO_3^{3-}, no changes at all are observed in any of the enamels. This evidence is consistent with XRD results since no crystalline borate compounds were found, probably due to the low amount of boron in the original frits. These results suggest, also, that the boron glassy matrix remains unchanged when Co-pigments are introduced since new devitrifying phases were not found. This experimental evidence is in accordance with the "structural similarity" between Co-glasses and matrices already observed for borate glasses, not containing SiO_2 [14].

3.2.2. Study of enamels prepared with frit C in the thermal interval 750–1000 °C

The enamels based on frit C were selected in order to evaluate the effect of the formulation on the firing behaviour of the glazes, concerning the Co(II) concentration and weight percentage of pigment, within the thermal range of interest for ceramic applications.

The XRD patterns and FTIR spectra of all the formulations and conditions detailed in Table 3, labelled as series C2, C3 and C4, were measured.

In order to analyze the phase changes during the blue glazing, in every thermal step, the relative intensity of the characteristic peaks of each crystalline compound expected to appear was measured, within the temperature range 750–1000 °C. Instrumental conditions were maintained constant in order to obtain a better comparison of the intensities of the same XRD characteristic lines by using "batch program" analysis in PC-APD software (version 3.6). Typical diffractions were selected as follows: Zn_2SiO_4, $d = 4.0240$ Å, $ZnAl_2O_4$, $d = 2.4380$ Å and ZnO, $d = 2.4759$ Å.

As may be observed in Fig. 5 for the representative series C2, ZnO prevails as crystalline phase in the whole thermal range until its disappearance, showing an abrupt descent around 800 °C, in coincidence with the maximum intensity of the peak corresponding to the phase Zn_2SiO_4. According to these results the phase $ZnAl_2O_4$ is estimated to be minor, in comparison with the other Zn-containing phases, in consistence with a low aluminium concentration in the original frit.

An identical behaviour is obtained when the analysis of evolution of phases is carried out for the rest of the series labelled C3 and C4. In all cases, for temperatures close to 1000 °C, the most characteristic peaks of the phases resulting from the interaction pigment–frit disappear. This evidence is understandable having in mind that the particles formed once the pigment is incorporated during formation of the enamel, loose their crystallinity by dispersion in the glassy borosilicate matrix.

The colorimetric parameters measurements were made on white ceramic biscuits glazed with the specimens of C3 and C4 compositions, obtained at 950 °C. The resulting values are shown in Table 4. Both colorimetric parameters *a* and *b* are within the range of typical pigments based on Co(II) silicate and aluminate, according to CIELab diagram for reference pigments [15].

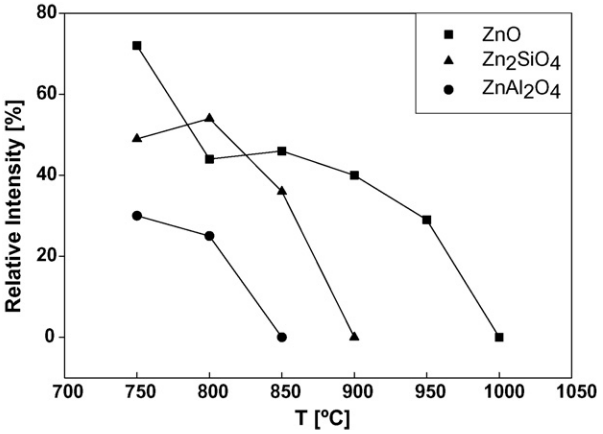

Fig. 5. Evolution of crystalline phases, according to XRD analysis, as a function of the firing temperature for batches of C2 series.

Table 4
Colorimetric parameters of representative glazes C3 and C4, obtained at 950 °C

Samples	*L*	*a*	*b*
C4-950	28.43	12.64	−33.41
C3-950	52.27	2.00	−19.93

3.2.3. Explanation of colours in enamels by electronic spectroscopy

In order to obtain more insight into the physical and chemical properties of the glazes their electronic (reflectance) spectra were investigated. The analysis of the spectra in the temperature range 750–1000 °C was carried out in an attempt to explain the origin of the change of colours when temperature rises.

The experimental results depicted in Fig. 6 are similar to those previously reported, for the related materials [1,16–18], showing that the pigment has two strong absorptions in the UV–visible domains. The band detected in the edge of the blue region (<500 nm) and in the 550–700 nm interval are assigned to the $^{4}A_2 \rightarrow {}^{4}T_1(^{4}F)$ and $^{4}A_2 \rightarrow {}^{4}T_1(^{4}P)$ electronic transitions of Co(II) cations ($3d^7$ high spin configuration) in tetrahedral site of W lattice of the pigment, respectively.

The "window" located at 520 nm, between the two mentioned bands, in the original pigment (corresponding to green in visible spectra) is shifted gradually to lower wavelength when the enamels are submitted to thermal treatment at elevated temperatures. Absorbance has the minimum value at 479 nm and 464 nm when temperature rises to 750 and 850 °C, respectively. In agreement with these results the observed colours for the corresponding enamels are green-blued and turquoise. Whereas, in the case of the blue glaze obtained at 950 °C, the visible light below 500 nm (blue) is mostly transmitted, as can be seen in the spectrum in Fig. 6, due to the shift of the blue edge band (located at <500 nm) assigned to $^{4}A_2(F) \rightarrow {}^{\circ 4}T_1(F)$ towards lower wavenumbers along with the enhancement of $^{4}A_2 \rightarrow {}^{4}T_1(^{4}P)$ electronic transition. The global evolution of the latter to a broad, high intensity band, in the visible region of 470–700 nm in this material, consisting of a triple signal, poorly resolved, around 521 nm (green region), 580 nm (yellow region) and 650 nm (red region), is characteristic of tetrahedral Co(II), distorted by Jahn–Teller effect [5]. This feature is interpreted as the presence of Co(II) ions in more distorted tetrahedral sites in the vitreous aluminosilicate environment which is responsible for the deeper blue colour of the glaze.

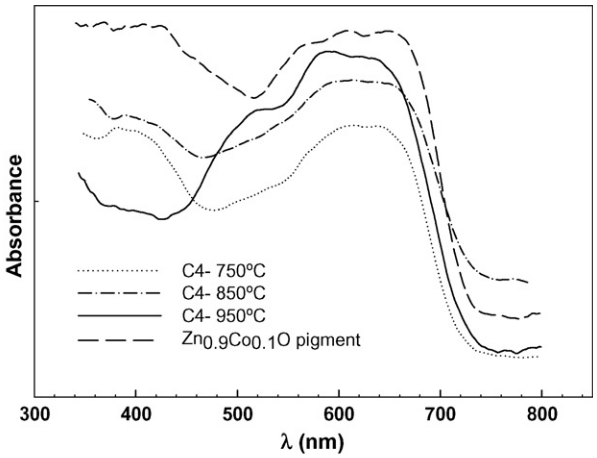

Fig. 6. UV–visible electronic spectra of C4 series, obtained at different temperatures, and Co-pigment.

4. Conclusions

- Mixed oxides of the Co(II)–ZnO system, with low concentration of Co(II), could be easily prepared and characterized, demonstrating to be potentially good blue pigments for ceramic industry.
- The phases formed during the enamelling, when the pigments were added to three different industrial ceramic frits, could be well characterized, structurally and espectroscopically, by combination of DRX and FTIR techniques.
- The most important interaction between pigment and frit when blue Co(II) coloration is developed, is due to the formation of crystalline compounds (as Zn_2SiO_4-willemite) involving SiO_2, the major constituent of the vitreous network in all the three commercial frits.
- One of the main differences, concerning the detection of phases formed with A, B, C-frits, is that in the case of B-enamel (containing $CaSiO_3$-wollastonite), the minor spinel $ZnAl_2O_4$ is undetected by FTIR analysis, whereas it is found in the A and C-enamels.
- The discussion of vibrational spectra has been particularly useful. The structural changes in the polyhedra, forming the network in system composed by amorphous and crystalline phases, have been studied by FTIR spectroscopy.
- Despite Co(II) content and their masses of pigment in the batches, the same crystalline Zn-silicate and Zn-aluminate are formed as a result of the pigment–frit interaction. Co(II) ions introduced in the SiO_4^{4-} and AlO_6^{3-} lattices, in substitution for Zn(II) ions, are responsible for the deep blue colour developed upon thermal treatment. Over 1000 °C, crystalline compounds vanish and cobalt ions in tetrahedral coordination remain dissolved in the glassy matrix.
- One of the major advantages of this way to obtain blue cobalt ceramic enamels is the ease of incorporation of Co(II) in the tetrahedral coordination site of Zn(II) in the structure of Zn_2SiO_4-willemite. This incorporation is facilitated by solid state reaction between $Co_xZn_{1-x}O$ pigments and the frits because Co(II) maintains the starting crystal site during enamelling.
- -The colorimetric parameters measured are in very good agreement with the structural and spectroscopic analysis presented.

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