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1 Titania Slag as Ceramic Pigment

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9 **10 Abstract**

11 Titania slag, a titanium ore obtained by smelting in reductant atmosphere ilmenite+rutile
12 mixes, consists mainly of a vitreous phase. Along with its principal use in titanium
13 dioxide production, it is being occasionally utilized to bestow a brown coloration on
14 ceramic tiles. Phase transformations and colouring mechanisms occurring during
15 ceramic processing were investigated by XRF-EDS, XRD, DRS and laboratory
16 simulation of application in glazed and unglazed tiles. Experimental data demonstrate
17 that titania slag transforms in pseudobrookite, undergoing a drastic colour change
18 during firing as a consequence of thermal oxidation with Fe²⁺ to Fe³⁺ and Ti³⁺ to Ti⁴⁺
19 reactions. The intense brown colour imparted by titania slag is stable in both low
20 temperature (up to 1050 °C) glassy coatings and high temperature (around 1200 °C)
21 glazes and bodies for porcelain stoneware tiles. In through-body application, titania
22 slag is particularly suitable to get 'spotting' effects.

23
24 **Key-words:** ceramic pigment; optical properties; pseudobrookite; titania slag.

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291. Introduction

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31 Titania slag is an important Ti ore, with a world output around 2 million of cubic tons per
32year [1]. It is obtained by smelting a mixture of ilmenite (FeTiO_3) and rutile (TiO_2) in order
33to enrich the Ti content of ilmenite (the most abundant titanium ore) and to improve the
34yield of successive processing steps [2-4]. In fact, titania slag is used in the TiO_2
35production by either hydrosulphuric acid dissolution [5-6] or chlorination [7].

36 The smelting process is carried out at temperatures around 1600 °C in a strongly
37reducing atmosphere, ensured by adding coal to Ti ores [2-4]. The slag, obtained by
38decrepitation [8], is to a large extent vitreous. The main crystalline phase is typically
39pseudobrookite, with minor residual rutile and ilmenite [9-11]. Pseudobrookite is a solid
40solution of $\text{Fe}^{2+}\text{Ti}^{4+}_2\text{O}_5$, $\text{Ti}^{4+}\text{Ti}^{3+}_2\text{O}_5$ and $\text{Ti}^{4+}\text{Fe}^{3+}_2\text{O}_5$ end terms, implying the occurrence of
41multiple valences of iron and titanium [9-10, 12-13]. Its stoichiometric composition is M_3O_5
42which is consistent with the compositional invariance observed in titania slags [14].
43However it has been shown that pseudobrookite appears as the main crystalline phase
44only when reduction of ilmenite is carried out at temperatures above 1200°C while rutile
45and ilmenite are the prevailing phases at temperatures below [15].

46 Titania slag easily undergoes thermal oxidation, involving Fe^{2+} to Fe^{3+} and Ti^{3+} to Ti^{4+}
47reactions [16-17]. Oxidation phenomena may occur even at low temperature [18] and are
48promoted by water vapour [17].

49 Although titania slag has been occasionally used in the latest years in the
50manufacturing of ceramic tiles to get low cost brown colours, no information is available in
51the literature on this new application. Therefore, the present study is aimed at
52understanding phase transformations, colouring mechanisms and technological behaviour
53of titania slag used as a ceramic pigment in the tilemaking process.

54

552. Experimental

56

57 A commercial titania slag, currently used in the ceramic tile industry, was sampled in the
58 form of rounded grains below 1 mm and characterized from the following viewpoints:

59– chemical composition by x-ray fluorescence energy dispersive spectrometry (XRF-EDS,
60 Link Analytical microprobe eLXI, 15 kV and 1 nA) as average of 3 sub-samples;

61– mineralogical composition by x-ray powder diffraction (XRPD, Bruker D8 Advance
62 equipped with solid state detector, Cu $K\alpha_{1,2}$ radiation, 10-100° 2θ , 0.02° step-scan, 13
63 s per step);

64– optical properties by diffuse reflectance spectroscopy (DRS, Perkin Elmer λ 35
65 spectrophotometer, 300-1100 nm range, 0.03 nm step-scan, BaSO₄ integrating sphere
66 and white reference material); reflectance (R_∞) was converted to absorbance (K/S) by
67 the Kubelka-Munk equation: $K/S=2(1-R_\infty) \cdot 2R_\infty^{-1}$.

68 Titania slag was tested as ceramic pigment into several glazes, glassy coatings and
69 bodies currently used in the tilemaking industry. For this purpose, it was dry ground in
70 agate mortar down to a particle mean diameter of 12 μm (80% wt. is in between 1 and 30
71 μm). This pulverized slag was added (5% wt.) to different glassy coatings (F1 to F4) and
72 glazes (S1 to S4). Furthermore, it was introduced (1% wt.) in porcelain stoneware bodies
73 (B1 and B2) either in pulverized form or as-received grains. The chemical and physical
74 characteristics of these ceramic matrices are reported elsewhere [19-20]. These tiles were
75 fast fired in an electric roller kiln in industrial-like conditions and characterized by DRS and
76 XRD. The technological potential of titania slag was assessed by comparing its colouring
77 performance in ceramic applications with high-quality, brown-reddish pigments used by the
78 tilemaking industry [21-22]: (Ti,Cr,W)O₂ *tobacco* rutile (*abr.* RT), (Fe,Zn)(Cr,Fe,Al)₂O₄ *tan*
79 spinel (ST), Fe₂O₃ *maroon* hematite (HM), (Cr,Fe)₂O₃ *dark brown* eskolaite (EB), and
80 Fe₂O₃-ZrSiO₄ *coral* zircon (ZC).

81

823. Results and discussion

83

843.1. Characteristics of titania slag

85

86 The titania slag utilized in the tilemaking industry contains approximately 62% TiO₂ and
87 32% FeO, with Si, Al, and Mn as main impurities (Table 1). Thus it is classified as low-Ti
88 slag with a Fe/Ti ratio close to the Fe_{0.32}Ti_{0.68} eutectics along the FeO-Fe₂O₃-TiO₂ join [12,
89 23].

90 Ilmenite and rutile are the main crystalline compounds found in the titania slag under
91 investigation; a minor amount of anatase is also present. The occurrence of a remarkable
92 amount of glassy phase is denoted by the high background and particularly by the
93 characteristic hump in the 20-40 ° 2θ range of the diffraction pattern (Fig. 1). A rough
94 estimate of relative proportions of the crystalline phases, neglecting the abundant
95 amorphous component, are: 43 % ilmenite, 47 % rutile, 10 % anatase. All these crystalline
96 phases exhibit a very low degree of structural order, inferred by their very broad lines that
97 do not permit any reliable determination of unit cell dimensions. It is likely that ilmenite and
98 a small fraction of rutile are relics of primary ores, while most of rutile has been produced
99 during the ilmenite reduction. Furthermore, very little information can be gained on the
100 short range order of the amorphous phase which might resemble the one expected for
101 pseudobrookite-like structures with M₃O₅ stoichiometry. The absence of well developed
102 crystalline pseudobrookite phases can be explained by a relatively lower than usual
103 temperature of processing achieved by the titania slag material under study [15].

104 The main optical feature of titania slag is the intense light absorption all over the
105 spectrum, with a maximum reflectance in the 11000-15500 cm⁻¹ range, that justifies its

106dark colour with a reddish cast (Fig. 2). This strong absorbance is due to both d-d electron
107transitions and charge transfer phenomena [24-25], particularly the ${}^5T_{2g}({}^5D) \rightarrow {}^5E_g({}^5D)$
108transition of octahedrally-coordinated Fe^{2+} in ilmenite, that is able to explain the light
109absorption below 12000 cm^{-1} , and the ${}^2T_{2g}({}^2D) \rightarrow {}^2E_g({}^2D)$ transition of Ti^{3+} in six-fold
110coordination, in defective rutile and/or ilmenite, which the bands in the $15000\text{--}22000\text{ cm}^{-1}$
111range may be attributed. Moreover, a $Ti^{3+} \rightarrow Ti^{4+}$ intervalence charge transfer (IVCT) may
112occur in both ilmenite and rutile, accounting for the intense band at $\sim 20000\text{ cm}^{-1}$, and a
113metal-ligand charge transfer (MLCT), like Fe-O and/or Ti-O, is responsible for the
114absorbance at high energies, peaking at $\sim 25000\text{ cm}^{-1}$.

115 This picture confirms that most iron and titanium is in the reduced form (Fe^{2+} and Ti^{3+}
116[9-10]) even if a significant amount of Fe^{3+} and Ti^{4+} cannot be ruled out on the basis of
117optical spectroscopy.

118

1193.2. Colouring mechanism

120

121 Titania slag undergoes a drastic colour virage once applied in ceramic matrices, that
122essentially consists in a slope change in the optical spectra (Fig. 3). This implies a
123decreased absorbance at low energies ($9000\text{--}18000\text{ cm}^{-1}$) that roughly corresponds to an
124increased emission of red to yellow wavelengths, so explaining the brown coloration
125bestowed on ceramic wares. However, the spectral features are quite similar in every
126ceramic matrix, the main difference being the light absorbance, decreasing from glassy
127coatings to glazes and down to porcelain stoneware bodies (Fig. 3).

128 This colour change is connected with phase transformations occurring to titania slag
129during the firing process of ceramics. The XRD patterns of glassy coatings (Fig 4) fired at
130750 °C (F4) and 1000 °C (F1) show that the fraction of crystalline phases in these samples
131is negligible. This can be due either to a dilution effect or to dissolution of the crystalline
132phases belonging to the titania slag. On the contrary, the XRD pattern of the floor tile glaze
133fired at 1200 °C (S1) show the occurrence of abundant anorthite (from the ceramic matrix)
134together with pseudobrookite (Fig. 4). This suggests that a significant recrystallization of
135both crystalline and amorphous phases from the slag has occurred.

136Optical spectroscopy shows the disappearance of absorption bands attributable to Ti^{3+} and
137 Fe^{2+} , that are replaced by others, referable to Fe^{3+} in octahedral coordination, hence
138probably hosted into the pseudobrookite structure [24-25]. Such bands are the Fe^{3+} d-d
139transitions from the ground state ${}^6A_1({}^6S)$ to 4T_1 , 4T_2 and ${}^4E+{}^4A$ (4G) as well as to 4T_2 and 4E
140(4D), shown in Figures 5A and 5B. A paired transition is present at $\sim 19000\text{ cm}^{-1}$, due to
141magnetically coupled Fe^{3+} ions located in adjacent sites, even if a possible contribution
142from the $Ti^{3+} \rightarrow Ti^{4+}$ IVCT cannot be ruled out. Furthermore, there are optical effects related
143to $Fe^{2+} \rightarrow Fe^{3+}$ IVCT, accounting for the weak absorption at the red-IR border, and both Fe-
144O and Ti-O MLCT at high energy.

145 This optical pattern is clearly the consequence of thermal oxidation involving especially
146pseudobrookite, that is likely to transform from a $Fe^{2+}Ti^{4+}_2O_5\text{--}Ti^{4+}Ti^{3+}_2O_5$ solid solution
147toward a composition close to the $Ti^{4+}Fe^{3+}_2O_5$ end term. As a matter of fact, the spectra of
148titania slag-added glazes are quite similar to that of synthetic pseudobrookite [26], besides
149some difference is appreciable particularly at low wavenumbers (Fig. 5C). It may be
150attributed to the occurrence in titania slag of more pronounced intervalence effects, such
151as $Ti^{3+} \rightarrow Ti^{4+}$ and $Fe^{2+} \rightarrow Fe^{3+}$ at about 19000 and 13500 cm^{-1} respectively.

152

1533.3. Colouring performance

154

155 The changes in the optical spectra have repercussions on colour saturation – that fastly
156decreases from chocolate brown (e.g. glassy coating F2) to light maroon (e.g. glaze S1)
157to beige (e.g. body B1) – and the a^* and b^* colourimetric parameters (Table 2).

158 Titania slag has a suitable behaviour in both low temperature (glassy coatings fired in
159the 800-1050 °C range) and high temperature applications (porcelain stoneware glaze S1,
160fired at 1200 °C). Its colour performance is deteriorated once temperatures over 1200 °C
161or very aggressive matrices (as the Ca- and Zn-rich glazes S2 and S3) are used. At all
162events, this is a common behaviour of ceramic pigments and especially of brown
163colorants, as it can be observed in Figure 6, where the variation of CIE L*, a* and b*
164parameters are plotted versus the firing temperature.

165 Ceramic coatings containing titania slag exhibit a noteworthy increase of brightness (L*
166values) for growing temperatures; however, this trend is superimposed to those of
167industrial pigments, that all suffer the same loss of colour saturation, but the dark brown
168EB (Fig. 6). On the other hand, titania slag undergoes to limited chromatic changes with
169increasing temperature, represented by a slight decreasing of the red component (a*) and
170a more pronounced increasing of the yellow one (b*) implying a colour virage toward an
171orange brown. At all events, similar trends are shown by RT, HM and ZC industrial
172pigments too (Fig. 6).

173 Unglazed floor tiles (porcelain stoneware) are usually coloured by through-body
174application involving pigment mixing together with raw materials [21-22]. Once applied in
175the pulverized form, titania slag gave rise to a pale brown coloration (Table 2). In contrast,
176it is able, when added in grains <1 mm, to impart an aesthetic 'spotting' effect, that is
177endeavoured to reproduce some features of natural stones [22].

178

1794. Conclusions

180

181 Titania slag is currently used like a pigment in the manufacturing of ceramic tiles to get
182low cost brown colours. Its colouring mechanism is due to changes in valences of
183transition metals hosted in the crystalline (ilmenite and TiO₂ polymorphs in the sample
184under investigation) and amorphous phases.

185 During ceramic firing, the crystalline and amorphous phases in the slag undergo
186thermal oxidation with (re)crystallization of pseudobrookite. This involves Ti³⁺ to Ti⁴⁺ and
187Fe²⁺ to Fe³⁺ reactions, leading to appearance in the optical spectra of typical d-d transitions
188of Fe³⁺ in octahedral coordination and a paired enhancement transition of magnetically
189coupled Fe³⁺ ions occurring in adjacent crystallographic sites. Absorbing most of the green
190to violet light, these bands provoke a colour virage to reddish brown. An additional optical
191band in the red region, likely due to Fe²⁺ → Fe³⁺ IVCT, is responsible of the dark shade.

192 Titania slag gives rise to an intense brown coloration in low temperature (800-1050 °C)
193glassy coatings and a suitable light maroon in high temperature (~ 1200 °C) glazes for
194porcelain stoneware tiles. The decrease of colour performance is connected with a
195progressive decomposition of pseudobrookite as temperature increases. Such a
196decomposition is accelerated in aggressive media, such as Ca- and Zn-rich glazes used
197at intermediate temperatures (1100-1150 °C) in the production of wall tiles. The colour
198performance of titania slag in through-body application is scarce when introduced in
199pulverized form, but it is appropriate to give desired 'spotting' effects once added in as-
200received grains.

201

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Table 1
Chemical composition of titania slag.

	Average (% wt.)	Standard deviation
TiO ₂	64.46	0.84
FeO _{tot}	30.49	0.72
SiO ₂	1.74	0.23
Al ₂ O ₃	1.43	0.11
MnO	1.06	0.15
CaO	0.33	0.09
MgO	0.30	0.02
V ₂ O ₅	<0.3	
CoO	<0.2	
Cr ₂ O ₃	<0.1	
Total	99.80	

242

243

Table 2

244

CIE L* a* b* parameters of ceramic matrices coloured with titania slag.

245

Ceramic matrix	Application	Firing temperature (°C)	CIE Lab parameters		
			L*	a*	b*
Glassy coatings	F4 third fire	750	39.32	3.31	3.96
	F3 third fire	900	37.08	7.63	10.22
	F2 wall tiles	950	33.26	6.62	6.53
	F1 wall tiles	1000	38.90	6.50	10.21
Glazes	S3 wall tiles	1100	58.12	3.86	6.73
	S2 floor tiles	1150	55.66	3.05	13.01
	S1 floor tiles	1200	50.16	5.55	13.03
	S4 sanitaryware	1250	70.51	1.82	15.22
Porcelain stoneware bodies	B1 floor tiles	1200	64.98	3.29	12.27
	B2 floor tiles	1200	63.07	2.98	11.97

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247

248 **Figure captions**

249

250 ~~Fig. 1. XRD pattern of titania slag.~~

251

252 ~~Fig. 2. Diffuse reflectance spectrum of titania slag with deconvolution of the~~
253 ~~main optical bands.~~

254

255 ~~Fig. 3. Diffuse reflectance spectra of slag-bearing glassy coatings (F1 to F4),~~
256 ~~glazes (S1 to S4) and porcelain stoneware bodies (B1 and B2).~~

257

258 ~~Fig. 4. XRD patterns of (a) floor tile glaze S1 and (b) glassy coatings F1 (upper)~~
259 ~~and F4 (lower) containing titania slag.~~

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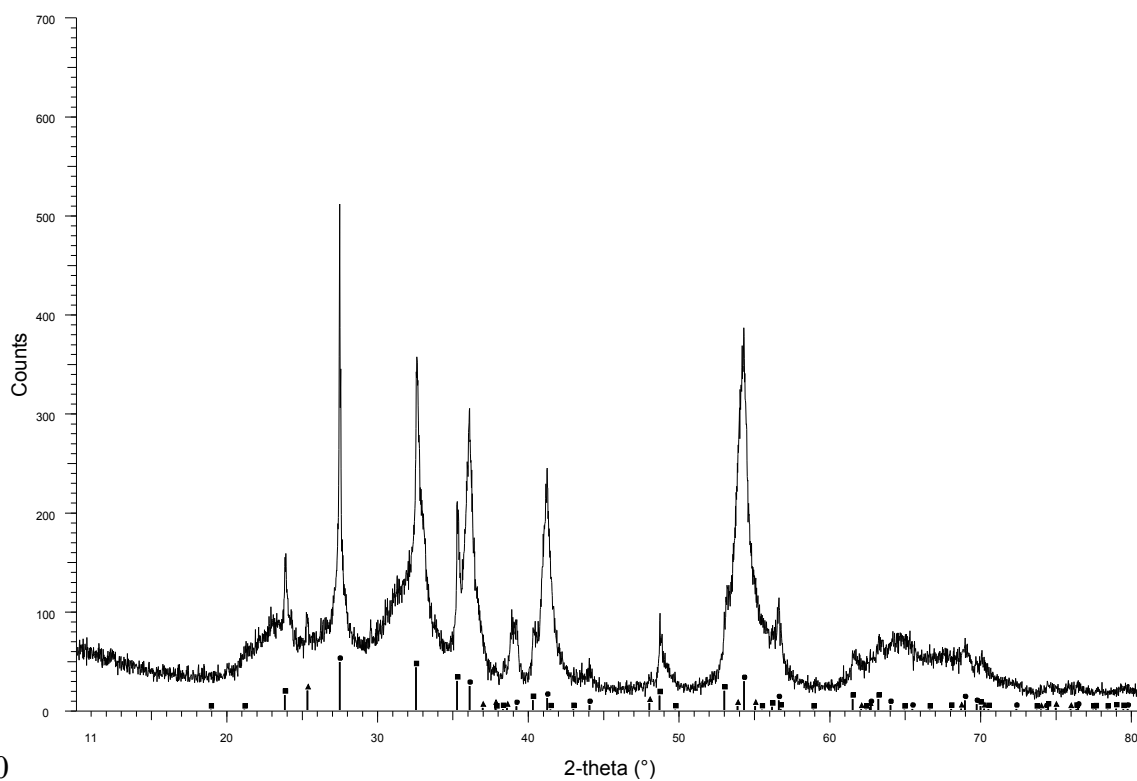
261 ~~Fig. 5. Diffuse reflectance spectra of (A) the glassy coating F2 and (B) the glaze~~
262 ~~S1, both containing titania slag, with deconvolution of the main optical bands.~~
263 ~~(C) Comparison with optical spectrum of pure pseudobrookite [26].~~

264

265 ~~Fig. 6. Chromatic changes versus firing temperature of glazes and glassy-~~
266 ~~coatings added with titania slag and industrial ceramic pigments. CIE-~~
267 ~~colourimetric parameters L^* (A), a^* (B) and b^* (C).~~

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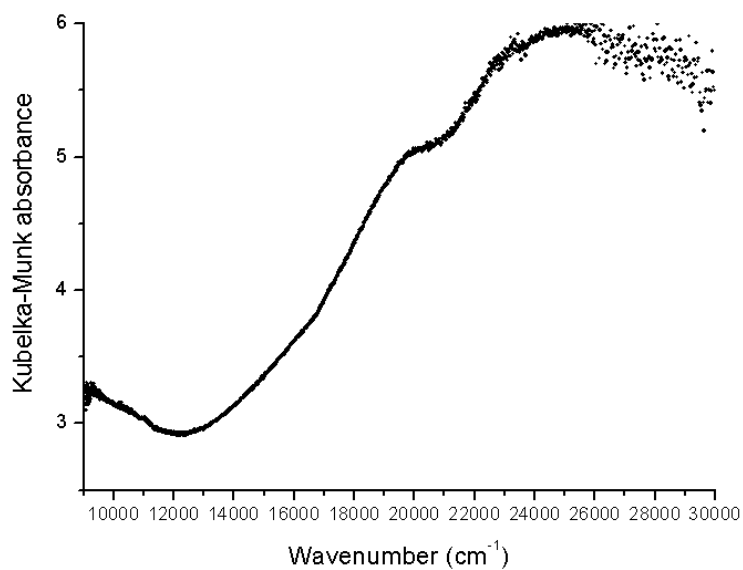


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272 [Fig. 1](#)

[Fig. 1. XRD pattern of titania slag..](#)



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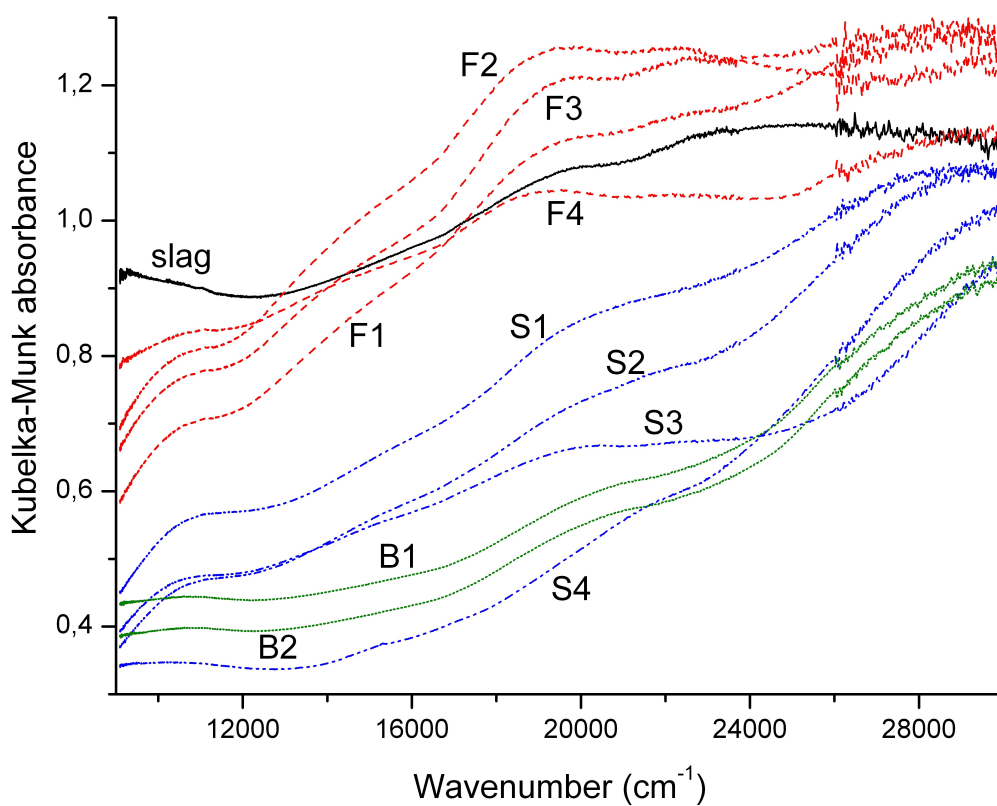
274 [Fig. 2. Diffuse reflectance spectrum of titania slag with deconvolution of the](#)
 275 [main optical bands.](#)

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Fig. 2

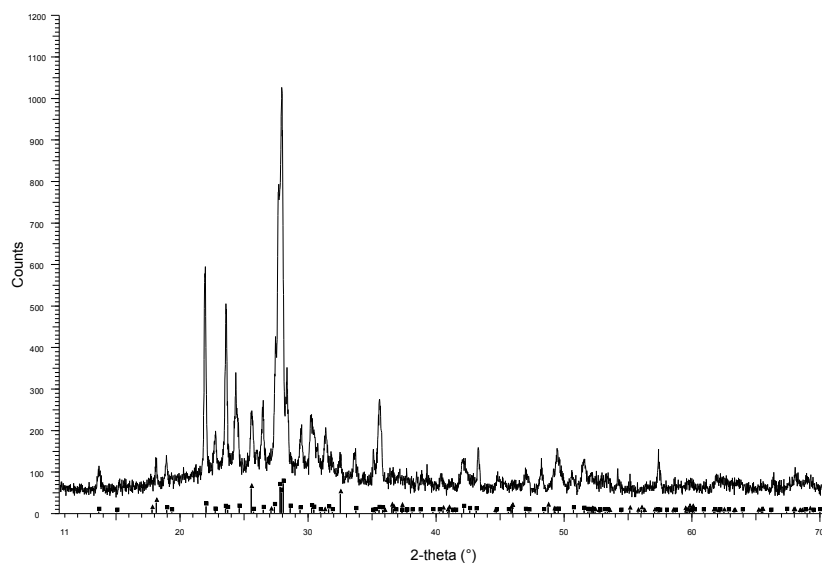


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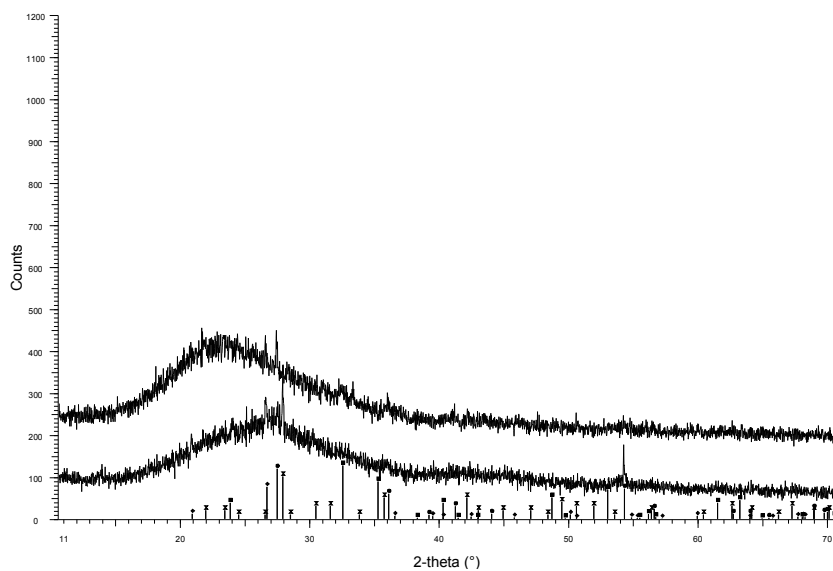
280 [Fig. 3. Diffuse reflectance spectra of slag-bearing glassy coatings \(F1 to F4\),](#)
281 [glazes \(S1 to S4\) and porcelain stoneware bodies \(B1 and B2\).](#)

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[Fig-3](#)



283



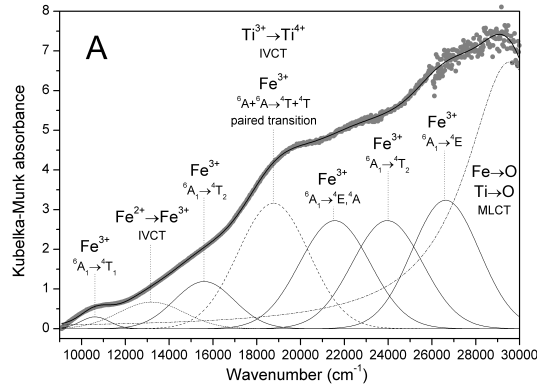
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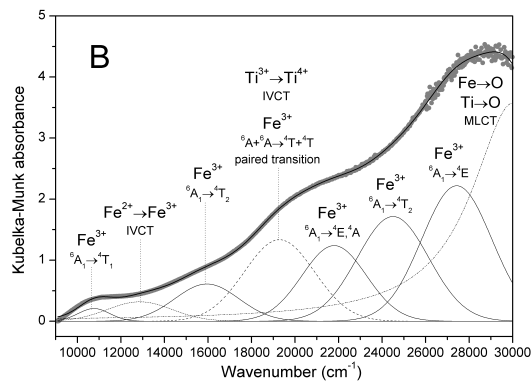
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Fig. 4

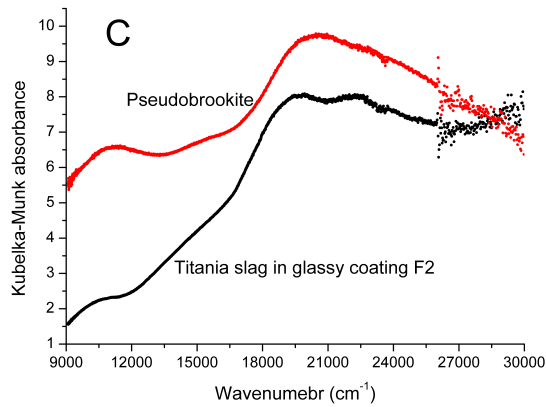
287 [Fig. 4. XRD patterns of \(a\) floor tile glaze S1 and \(b\) glassy coatings F1 \(upper\)](#)
288 [and F4 \(lower\) containing titania slag.](#)



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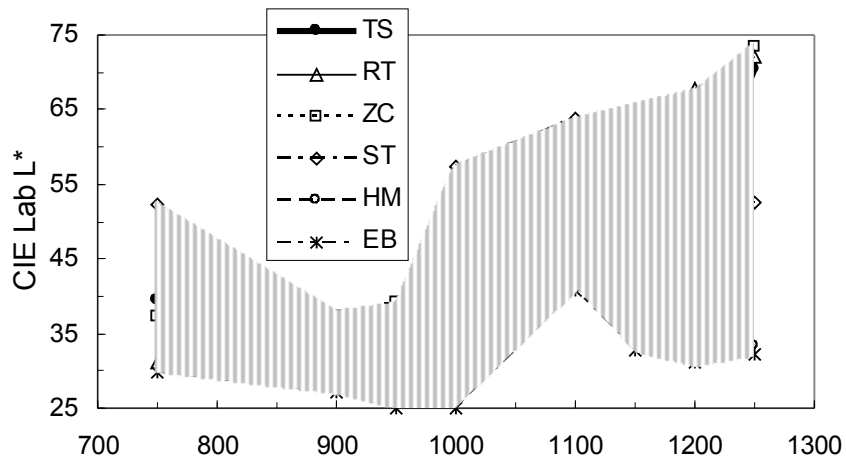
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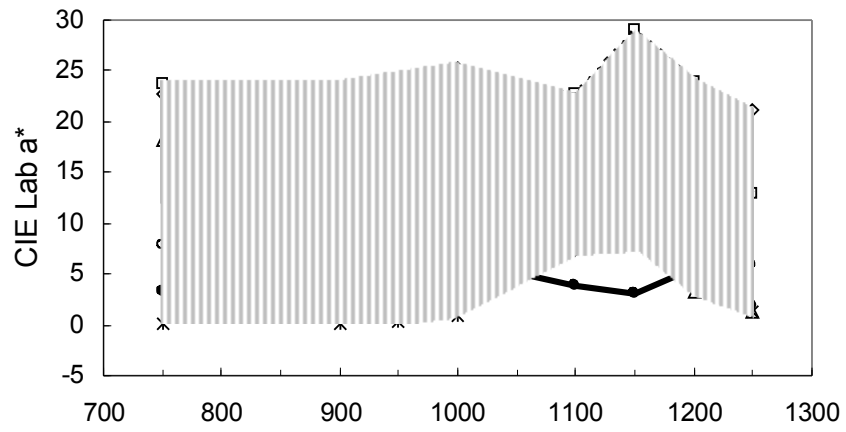
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 295 [\(C\) Comparison with optical spectrum of pure pseudobrookite \[26\].](#)

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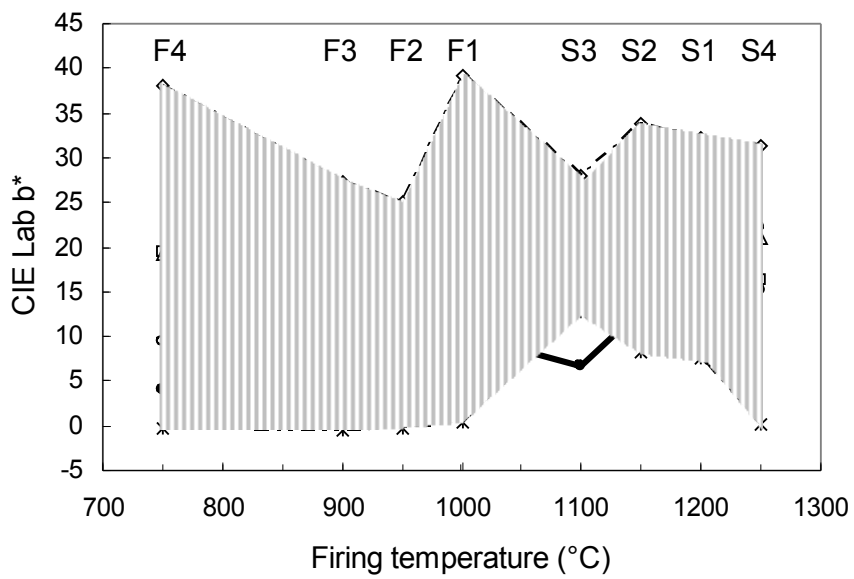
Fig. 5



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301 [Fig. 6. Chromatic changes versus firing temperature of glazes and glassy](#)
302 [coatings added with titania slag and industrial ceramic pigments. CIE](#)
303 [colourimetric parameters L* \(A\), a* \(B\) and b* \(C\).Fig-6](#)