Multitechnique approach to V–ZrSiO$_4$ pigment characterization and synthesis optimization

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Available online 23 June 2006

Abstract

The synthesis of blue-turquoise V–ZrSiO$_4$ pigment from an aqueous solution of Na$_2$O·2.5SiO$_2$·5H$_2$O (soluble glass) and the citrate complexes of zirconium and vanadium was investigated as a function of V$_2$O$_5$ contents, mineralizers (NaF and/or LiNO$_3$) addition and thermal cycle. Blue V–ZrSiO$_4$ was obtained without mineralizers addition for the (ZrO$_2$)(SiO$_2$)(V$_2$O$_5$)$_{0.09}$ composition; QPA analysis shows that a thermal cycle 3 h long, $T_{max} = 800\,^\circ$C, can lead to a 78.0 wt.% of ZrSiO$_4$. The addition of mineralizers gave rise to 73.0 wt.% of ZrSiO$_4$ for the (ZrO$_2$)(SiO$_2$)(NaF)$_{0.16}$(V$_2$O$_5$)$_{0.09}$(LiNO$_3$)$_{0.09}$ composition and a thermal cycle 2 h long, $T_{max} = 800\,^\circ$C. LiNO$_3$ can favour both ZrSiO$_4$ formation and a fairly blue colour, up to LiNO$_3$ = 0.09 moles; NaF seems effective on ZrSiO$_4$ formation only when mixed with LiNO$_3$ through the formation of LiF. HT-XRD analysis of this composition agrees with QPA results at the corresponding temperature; ZrSiO$_4$ was present (64.0 wt.%) at 730 $^\circ$C and good colour parameters were obtained.
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Keywords: Blue-turquoise pigment; Powders-solid-state reaction; X-ray methods; Colour

1. Introduction

The blue-turquoise V–ZrSiO$_4$ pigment has been extensively studied since its discovery in 1948.[1] The industrial synthesis takes place by means of a solid-state reaction at about 800–1050 $^\circ$C, by addition of mineralizers (NaF, NaCl) and by carrying out an appropriate thermal cycle,[2,4] whose length can range from 4 to 24 h. The reagents are SiO$_2$, ZrO$_2$ in a molar ratio slightly greater than 1 and a V$_2$O$_5$ font, such as NH$_4$VO$_3$; the amount of V$_2$O$_5$ can correspond to ≈3 wt.% (≈0.02 mol) with respect to ZrSiO$_4$. The different synthetic methods can be classified as: wet methods in hydroalcoholic medium, sol–gel method or heterogeneous synthesis in the case of using an aqueous suspension of colloidal silica. In the first case, tetraethyl orthosilicate, zirconium propoxide and vanadium (IV) oxyacetylacetonate were the reagents; in the second one zirconium (IV) acetate and vanadium (IV) oxyacetylacetonate were added to an aqueous suspension of colloidal silica.[3] Other syntheses can be considered as simple variations of those methods.[4–7] In all cases, the development of a final blue colour at a temperature lower than 1000 $^\circ$C required the use of mineralizers (NaF). As final product these syntheses gave ZrSiO$_4$, as indicated by XRD results, and the colour was classified as blue. In view of the importance of this system and with the aim to propose an alternative way to the conventional synthesis of blue turquoise V–ZrSiO$_4$ pigment, this work focuses on the synthesis and characterization of blue-turquoise pigment obtained from an aqueous solution of Na$_2$O·2.5SiO$_2$·5H$_2$O (soluble glass) and citrate complexes of zirconium and vanadium. The study was carried out as a function of V$_2$O$_5$ content, mineralizers addition (NaF and/or LiNO$_3$) and thermal cycle. The best results, in term of blue colour and ZrSiO$_4$ yield, can be obtained at $T_{max} = 800\,^\circ$C, thermal cycle 3 h long, without mineralizers addition, composition (ZrO$_2$)(SiO$_2$)(V$_2$O$_5$)$_{0.09}$ with a 78.0 wt.% of ZrSiO$_4$ or at $T_{max} = 800\,^\circ$C with a short thermal cycle (2 h long), addition of mineralizer and composition (ZrO$_2$)(SiO$_2$)(NaF)$_{0.16}$(V$_2$O$_5$)$_{0.09}$(LiNO$_3$)$_{0.09}$ and 73 wt.% of ZrSiO$_4$ yield; the major factors in determining the ZrSiO$_4$ yield

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Table 1
Theoretical composition of precursors and thermal cycles used

Composition		Thermal cycles	
		Heating	Isothermal time (min)
$(ZrO_2)(SiO_2)(V_2O_5)_{0.03}$	S1	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(V_2O_5)_{0.09}$	S2	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(V_2O_5)_{0.09}$	S260	800 °C in 2 h	60
$(ZrO_2)(SiO_2)(V_2O_5)_{0.02}(LiNO_3)_{0.09}$	F1	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(NaF)_{0.08}(V_2O_5)_{0.02}(LiNO_3)_{0.09}$	F2	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(NaF)_{0.16}(V_2O_5)_{0.02}(LiNO_3)_{0.09}$	F3	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(NaF)_{0.24}(V_2O_5)_{0.02}(LiNO_3)_{0.09}$	F4	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(NaF)_{0.16}(V_2O_5)_{0.03}(LiNO_3)_{0.17}$	V1 = T1	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(NaF)_{0.16}(V_2O_5)_{0.09}(LiNO_3)_{0.17}$	V2	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(NaF)_{0.16}(V_2O_5)_{0.16}(LiNO_3)_{0.17}$	V3	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(NaF)_{0.16}(V_2O_5)_{0.24}(LiNO_3)_{0.17}$	V4	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(V_2O_5)_{0.03}$	L1 = S1	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(V_2O_5)_{0.03}(LiNO_3)_{0.09}$	L2	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(V_2O_5)_{0.03}(LiNO_3)_{0.17}$	L3	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(V_2O_5)_{0.03}(LiNO_3)_{0.35}$	L4	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(V_2O_5)_{0.03}$	N1 = S1	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(V_2O_5)_{0.03}(NaF)_{0.08}$	N2	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(V_2O_5)_{0.03}(NaF)_{0.16}$	N3	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(V_2O_5)_{0.03}(NaF)_{0.24}$	N4	800 °C in 2 h	1
	T0	700 °C in 2 h	1
	T1	800 °C in 2 h	1
$(ZrO_2)(SiO_2)(NaF)_{0.16}(V_2O_5)_{0.03}(LiNO_3)_{0.1}$	T2	900 °C in 2 h	1
	T3	1000 °C in 2 h	1
	T4	1200 °C in 2 h	1
	ZV4 w/uw	800 °C in 2 h	4
	ZV60	800 °C in 2 h	60
$(ZrO_2)(SiO_2)(NaF)_{0.16}(V_2O_5)_{0.09}(LiNO_3)_{0.09}$	ZV530	530 °C in 1 h 50.5 min	60
	ZV730	730 °C in 3 h 10 min	60
	ZV930	930 °C in 5 h 30 min	60

are thermal cycle, mineralizers (type and content) and amount of V_2O_5.

2. Experimental procedure

2.1. Preparation of precursors

$ZrOCl_2\cdot 8H_2O$ was dissolved in H_2O (50 mL, 0.01 mol/L), afterwards an aqueous solution of citric acid was prepared (50 mL, 0.02 mol/L). The Zr(IV) solution was added to the citrate solution and the pH was corrected to 3 by adding NH_4OH (6 mol/L). A $Na_2O\cdot 2.5SiO_2\cdot 5H_2O$ (soluble glass) solution was mixed to that of Zr(IV)-citrate in a 1:1 Zr/Si molar ratio. At this stage the mineralizers (NaF and/or $LiNO_3$) were added in the desired amount. NH_4VO_3 was dissolved in H_2O (50 mL, 0.001 mol/L) and mixed with an aqueous solution of citric acid in a V/citric acid molar ratio = 1:2. Finally the V–citrate solution was added to the Zr(IV)–citrate–SiO_2 solution in order to obtain a $V_2O_5:ZrO_2$ molar ratio in the 0.02–0.24 range. The solution turned blue and was concentrated to small volume by boiling. Upon heating the solution formed a gel that was completely dried in an oven at 150 °C. This precursor was hand-ground in an agate mortar. The theoretical compositions of precursors and the thermal cycles utilized were summarized in Table 1.

2.2. Sample characterization

Reactions among raw materials, mineralizers effect and structural evolution were followed by using a multitechnique approach. The experimental details of data collection for the X-ray diffraction (XRD) analysis are reported as supplementary materials. The powders of each samples were mounted on a flat Al holder and data collection were performed in a conventional Bragg-Brentano (BB) parafocusing geometry. The identified phases[8] with their counts and relative intensity are reported in Tables 2, 3a and 3b. QPA (quantitative phase analysis) with XRD is performed by using the combined Rietveld[9–11] and reference intensity ratio (RIR) method,[12] which enables the calculation of both the crystalline and amorphous fraction in a mixture. A known amount of spike (corundum NIST SRM 674a, 10 wt.%) is added to the unknown mixture and considered as a component itself. Refinements of the powder spectra were performed by using GSAS software package.[13] The starting structure models were taken from the literature.[14] For each refinement the following parameters were refined: Chebyshev polynomial background function with a variable number of coefficients, zero-shift correction, a Gaussian and a Lorentzian coefficient of the pseudo-Voigt peak-profile function, an offset function for the correction of the peak asymmetry, a sample-displacement parameter, the phase fraction and unit-cell param-

Table 2

Colour parameters, qualitative XRD results[a] of mixtures with nominal composition $(ZrO_2)(SiO_2)(NaF)_x(V_2O_5)_y(LiNO_3)_z$ heated at 800 °C, isothermal time 1 min and colour parameter of a commercial pigment

	L^*	a^*	b^*	Z		M		T		NaCl		C		Q		LS2		L2S		NS	
				Counts	I/I_0 (%)	Counts	I/I_0 (%)	Counts	I/I_0 (%)	Counts	I/I_0 (%)	Counts	I/I_0 (%)	Counts	I/I_0 (%)	Counts	I/I_0 (%)	Counts	I/I_0 (%)	Counts	I/I_0 (%)
$x=0$, $z=0$																					
$y=0.03$ S1	76	−3	−1	0	0	0	0	6200	100	1100	18										
$y=0.09$ S2	67	−15	−24	9700	100	2000	20	7000	74	3300	34	2500	26								
$x=0.16$, $z=0.17$																					
$y=0.03$ V1 = T1	75	−10	−11																		
$y=0.09$ V2	61	−15	−26	25000	100	400	2	0	0	7000	29	2800	11			140	1	180	1		
$y=0.16$ V3	62	−16	−21																		
$y=0.24$ V4	63	−15	−20	22400	100	600	3	0	0	2800	13	620	3								
$y=0.09$ V2 w				40000	100	400	1	100	0.2	380	1	5000	13					265	1		
$y=0.02$, $z=0.09$																					
$x=0$ F1	74	−11	−6	300	7	0	0	4200	100	2200	51			150	4						
$x=0.08$ F2	77	−11	−7	9400	100	300	3	4700	50	1400	15	420	4			380	4	85	1		
$x=0.16$ F3	75	−13	−10	13900	100	500	4	5200	38	2200	16	760	6			780	6	120	1		
$x=0.24$ F4	61	−14	−18	26000	100	1500	6	500	2	3000	11	182	1			210	1	250	1	170	1
$y=0.03$, $x=0$																					
$z=0$ L1 = S1	76	−3	−1	0	0	0	0	6200	100	1100	18										
$z=0.09$ L2	76	−11	−13	2100	8	500	3	10000	48	21000	100	580	3								
$z=0.17$ L3	77	−11	−11																		
$z=0.35$ L4	79	−9	−6	20000	100	950	5	5000	25	2200	11	1700	8			2200	10	230	1	2700	13
$y=0.03$, $z=0$																					
$x=0$ N1 = S1	76	−3	−1	0	0	0	0	6200	100	1100	18										
$x=0.08$ N2	77	−2	3																		
$x=0.16$ N3	78	−2	4																		
$x=0.24$ N4	79	−2	7	800	4	1130	6	19400	100	8300	43	1650	9								
Commercial pigment	65	−13	−20																		

[a] Abbreviations: Z, $ZrSiO_4$; T, t-ZrO_2; M, m-ZrO_2; Q, α-quartz SiO_2; C, cristobalite SiO_2; LS2, $Li_2Si_2O_5$; L2S, Li_4SiO_4; NS, Na_2SiO_3.

Table 3a

Colour parameters of mixtures with nominal composition $(ZrO_2)(SiO_2)$ $(NaF)_{0.16}(V_2O_5)_{0.03}(LiNO_3)_{0.17}$ at different temperatures (T series)

	L^*	a^*	b^*
T0	70	−7	−8
T1	75	−10	−11
T2	70	−12	−20
T3	72	−11	−17
T4	79	−6	−6

Table 3b

HT-XRD results[a] (intensity counts) of mixture with nominal composition $(ZrO_2)(SiO_2)(NaF)_{0.16}(V_2O_5)_{0.09}(LiNO_3)_{0.09}$

	Z	T	M	NaCl	Q
25 °C	0	151	1406	1089	0
330 °C	0	125	1521	605	0
530 °C	0	96	1498	894	77
630 °C	0	130	1436	900	44
730 °C	112	174	1384	847	55
830 °C	562	94	1136	718	69
930 °C	3091	234	369	106	0
1130 °C	2894	188	428	123	0

[a] Abbreviations: Z, $ZrSiO_4$; T, t-ZrO_2; M, m-ZrO_2; Q, α-quartz SiO_2.

eters of each phase. The cut-off value for the calculation of the peak profiles in all refinement was 0.1%. The results of QPA are reported in Table 4; values of the refined unit-cell parameters and volume are reported in Table 5. Agreement indices and figures with the comparison of the observed and calculated XRD profiles obtained by QPA analyses are available as supplementary materials; $R(F^2)(\%)$ is in the range 3–13%. Scanning electron microscopy (SEM) analysis was performed with a Philips XL-30 instrument equipped with a energy dispersive X-ray analyser (EDS, X_EDS Edax9900). UV-vis spectra in the

190–1800 nm spectral range, were obtained with a Perkin-Elmer Lambda 19 spectrophotometer, by using the diffuse reflectance technique and a $BaSO_4$ plate as reflectance standard. Colour parameters were evaluated by means of CIELAB[15] method by using the PECOL software and were summarized in Tables 2–4. Some samples were washed, both to eliminate undesirable solu-

Table 4

Colour parameters and QPA results[a,b] (wt.%)

	L^*	a^*	b^*	Z	T	M	Q	C	LS2	NaCl	LiCl	LiF	NVO	Amorphous amount
ZV4 uw	63	−16	−24	73.0	1.0	1.5	2.0	2.0		10	0.5			10.0
ZV4 w				85.0	0.5	1.0	11.0	1.0						1.5
ZV4 uw[c]	60	−19	−25											
ZV4 w[c]	62	−18	−27											
ZV60	69	−15	−25	76.5	1.0	1.5			1.0	8.5			1.5	10.0
S260	64	−15	−25	78.0	1.5	2.0		4.5		6.0				8.0
Commercial	65	−13	−20											
Commercial[c]	54	−18	−31											
ZV530	78	−1	16		51.0					9.0		3.0		37.0
ZV730	61	−15	−25	64.0	2.0	1.5			2.0	8.0			0.5	22.0
ZV930	66	−13	−21	79.0	5.5	1.0			0.5	5.5	1.5		0.5	6.5

[a] Abbreviations and ICSD code: Z, $ZrSiO_4$ (100248); T, t-ZrO_2 (72949); M, m-ZrO_2 (18190); Q, α-quartz SiO_2 (34644); C, cristobalite SiO_2 (9327); LS2, $Li_2Si_2O_5$ (15414); NVO, $Na_{0.7}V_6O_{15}$ (38148).

[b] Maximum value of σ for each sample = 0.5%.

[c] Enamelled.

Table 5

Refined unit-cell parameters and volume for $ZrSiO_4$ and t-ZrO_2 calculated from QPA and literature values

	$ZrSiO_4$				
	$a(Å)$	$b(Å)$	$c(Å)$	$\alpha = \beta = \gamma(°)$	$V(Å^3)$
Lit[a]	6.6042(4)	6.6042(4)	5.9796(3)	90	260.8
ZV730	6.6066(1)	6.6066(1)	5.9836(1)	90	261.17(1)
ZV930	6.6054(1)	6.6054(1)	5.9817(1)	90	260.99(1)
ZV60	6.6043(1)	6.6043(1)	5.9816(1)	90	260.91(1)
S260	6.6049(1)	6.6049(1)	5.9821(1)	90	260.97(1)
ZV4 w	6.6067(1)	6.6067(1)	5.9865(1)	90	260.30(1)
ZV4 uw	6.6085(1)	6.6085(1)	5.9858(1)	90	261.41(1)
	t-ZrO_2				
	$a(Å)$	$b(Å)$	$c(Å)$	$\alpha = \beta = \gamma(°)$	$V(Å^3)$
Lit.[b]	3.6067(4)	3.6067(4)	5.1758(8)	90	67.3
ZV530	3.5976(1)	3.5976(1)	5.2000(1)	90	67.31(1)

[a] Hazen, R. M. and Finger, L.W., *Am. Mineral.*, 1979, **64**, 196–201, in ref.[14].

[b] Martin, U., Boysen, H. and Frey, F., *Acta Crystallogr. B*, 1993, **49**, 403–413 in ref.[14].

ble salts and to measure the vanadium concentration leached from the pigment in the washing solution. For this purpose, 1 g of calcined powder was washed with 250 mL of 0.3 mol/L HNO_3 under magnetic stirring for 24 h and another 1 g of the same powder sample was washed with 250 mL of H_2O in the same conditions. The determination of the concentration of leached ions was performed with an ICP spectrometer (Varian Liberty 200). Samples (10 wt.%) of ZV4 (both unwashed and washed) and of commercial pigment after manual grinding with a glossy glaze, were enamelled on a porcelainized tile at 900 °C.

3. Results and discussion

3.1. Synthesis without addition of mineralizers

The samples $(ZrO_2)(SiO_2)(V_2O_5)_{0.03}$ (S1) and $(ZrO_2)(SiO_2)(V_2O_5)_{0.09}$ (S2) presented different colours, the first was white-grey and the second one blue; their UV-vis spectra were consistent with these findings, in fact only the spectrum of S2 was different from that of simple $ZrSiO_4$ and presented the absorption band at 625 nm and a high transmission at ≈400 nm. As a consequence the colour parameters were typical of a blue colour and were better than those of commercial pigment (Table 2). The XRD spectra were consistent with these results; spectrum of S1 showed only the peaks belonging to those of t-ZrO_2 and was, as a whole, characteristic of poorly crystalline species. While spectrum of S2 showed a better resolution and in order of relative intensity decreases it was recognized: $ZrSiO_4$, t-ZrO_2, NaCl, SiO_2 (cristobalite) and m-ZrO_2. The starting solution contained a great amount of sodium and chloride ions deriving from the SiO_2 and ZrO_2 fonts, this explained that NaCl was normally present in all XRD spectra. Both the previous samples contained the same theoretical moles of SiO_2 and ZrO_2, and, as a consequence the same amount of NaCl; the different results about the formation of $ZrSiO_4$ clearly indicated the ineffectiveness of NaCl as mineralizer. This might be due to the limited ability of NaCl to react with SiO_2 in view of the higher bond energy of Si–O by respect to Si-Cl,[16] so preventing the formation of phases during the thermal treatment. On the other hand these results confirmed the ability of V_2O_5 to act as mineralizer[17] favouring zircon formation, which started before 800 °C. The colour parameters (Table 4) of S260 (S2 maintained for 1 h at 800 °C) were almost unchanged with respect to S2 (Table 2); XRD spectrum was typical of highly crystalline species and from QPA results (Table 4) the $ZrSiO_4$ yield was 78.0 wt.% with small amount of other oxides. The similarity of colour parameters of S2 and S260 suggested that, in the former, $ZrSiO_4$ was not crystallized very well and might be a main component of the amorphous phase. This result is very important because it states, for the first time, that it is possible to obtain good blue-turquoise pigment at low temperature, without mineralizers and in a very short time.

3.2. Effect of V_2O_5 content

The electronic spectrum of samples with starting composition $(ZrO_2)(SiO_2)(NaF)_{0.16}(V_2O_5)_x(LiNO_3)_{0.17}$, where $x = 0$–0.24,

showed a sharp absorbance increase in the 400–1100 nm spectral range going from $x = 0.03$ (V1) to $x = 0.09$ (V2); the maximum of transmission in the 400 nm region and the best L^*, a^*, b^* values for a blue colour (Table 2) were observed for V2 and these parameters were similar to those of S2 and S260. The XRD spectra of V2 and V4 did not show significant differences with varying the V_2O_5 content, in term of phases type and their peak counts. The identified crystalline phases, in order of relative intensity decrease, were: $ZrSiO_4$, NaCl, SiO_2 (cristobalite), m-ZrO_2, Li_4SiO_4 and $Li_2Si_2O_5$. $ZrSiO_4$ peak counts in the XRD spectrum of V2 were strongly higher with respect to those of S2; a reverse trend was observed for ZrO_2 peaks suggesting that this mixture of NaF and $LiNO_3$ is very useful in favouring the fast crystallization of $ZrSiO_4$ but the effect on the blue colour is significant only at low V_2O_5 content. Sample V2 was carefully washed with H_2O and its XRD spectrum showed that the peaks due to NaCl strongly diminished, while the peak counts of insoluble phases increased sharply.

3.3. Effect of mineralizers

We added the solution of raw materials with two types of mineralizers: NaF and $LiNO_3$. The role of lithium silicates, as mineralizer in solid-state reaction between SiO_2 (α-quartz) and ZrO_2, is well known[18] as well as that of V_2O_5[17] and NaF.[2–4] So in principle there were present three mineralizers: NaF, $LiNO_3$ and V_2O_5. The colour parameters of samples with varying $LiNO_3$ content (L series) $(ZrO_2)(SiO_2)(V_2O_5)_{0.03}(LiNO_3)_z$ $z = 0$–0.35 improved up to $z = 0.09$ (L2) and got worse for $z > 0.09$, (Table 2). The XRD spectrum of L2, showed $ZrSiO_4$ as a minor phase, NaCl and t-ZrO_2 were the main phases. The increase of $LiNO_3$ content seems to do not favour the blue colour despite of the high relative intensity of $ZrSiO_4$ peaks. In this condition a significant amount of lithium and sodium silicates was formed and their presence could negatively affect the b^* value. The NaF role was studied in the samples (N series) of composition $(ZrO_2)(SiO_2)(NaF)_x(V_2O_5)_{0.03}$ $x = 0$–0.24 and (F series) $(ZrO_2)(SiO_2)(NaF)_x(V_2O_5)_{0.02}(LiNO_3)_{0.09}$ $x = 0$–0.24. All colour parameters of F series decreased almost regularly with increasing NaF content, with an improvement in blue colour; the best results were for F4, whose XRD data showed the maximum value of peak counts for $ZrSiO_4$ and the minimum value for t-ZrO_2, (Table 2). The samples N2–N4 did show a pale yellow-green colour and the XRD spectrum of N4 showed $ZrSiO_4$ as a very minor species, the main phases being t-ZrO_2, NaCl and SiO_2 (cristobalite), indicating the ineffectiveness of NaF as mineralizer at a temperature as low as 800 °C; because the solid-state reaction between NaF and SiO_2 at this temperature is slow. Nevertheless the addition of 0.24 mol of NaF (N4) enables the formation of a little amount of $ZrSiO_4$ while its lacking (N1) does not.

3.4. Effect of temperature

A thermal treatment in the 700–1200 °C range (T series) was performed on samples of composition $(ZrO_2)(SiO_2)(NaF)_{0.16}(V_2O_5)_{0.03}(LiNO_3)_{0.17}$. The absorbance of the band at

625 nm was quite constant from 700 to 1000 °C and afterwards decreased dramatically; the electronic spectrum of sample T0 presented a very low transmission in the blue region and this was reflected by its colour parameters; the best values were calculated for sample T2 (Tables 3a and 3b). The colour changed from grey-blue (T0), to blue (T2, T3) and again to grey-blue (T4).

On the basis of colour parameters, $ZrSiO_4$ yield (73.0 wt.%) and mineralizers consumption we identified the composition $(ZrO_2)(SiO_2)(NaF)_{0.16}(V_2O_5)_{0.09}(LiNO_3)_{0.09}$ (ZV4) as the optimised one.

3.5. HT-XRD and QPA

The HT-XRD spectra of ZV4 (Table 3, HT-XRD spectra are available as supplementary materials) revealed that at 330 °C ZrO_2 (monoclinic or tetragonal) has been partly crystallized yet; no peaks were observed due to NaF, LiX or SiO_2, in line with the tendency of SiO_2 to form amorphous phases, this enhanced its reactivity promoting $ZrSiO_4$ formation at low temperature. A slow heating rate enables α-quartz SiO_2 crystallization at 530 °C; the peak counts of its main signal changed little with temperature and disappeared above 830 °C. The peaks counts of ZrO_2 and SiO_2 are almost unchanged until $T > 830$ °C and this suggests that $ZrSiO_4$ is mainly formed through reaction of ZrO_2 and SiO_2 from the amorphous phase; above 830 °C the peak counts of m-ZrO_2 decrease and those of SiO_2 disappear so indicating the $ZrSiO_4$ formation involves crystalline oxides. We chose the temperature values of 530 and 730 °C, corresponding to the appearance in HT-XRD powder spectra of the peaks of SiO_2 and $ZrSiO_4$, for performing on sample ZV the same thermal cycle as in HT-XRD and for carrying out the QPA and colour parameters calculation (ZV530, ZV730, ZV930); QPA was performed also on a sample heated at 930 °C because HT-XRD indicated that at this temperature $ZrSiO_4$ counts reach the maximum value and ZrO_2 the minimum one. QPA (Table 4) for ZV4 and S260 confirmed the presence of $ZrSiO_4$, several crystalline species and revealed also a significant amount of amorphous phase. After washing of ZV4, in its XRD spectrum are not identified lines of any soluble species, while a little amount of amorphous phase was still present. The length of isotherm (ZV60) slightly affected the yield of $ZrSiO_4$ that increased up to 76.5 wt.%; SiO_2 disappeared, while $Li_2Si_2O_5$ and $Na_{0.7}V_6O_{15}$ $(Na_{0.7}V_{0.7}{}^{IV}V_{5.3}{}^{V}O_{15}$, Bannermanite) were also identified. The amorphous amount was almost unchanged. The QPA analysis excluded the presence of NaF in both case. The calculated cell parameters of $ZrSiO_4$ (Table 5) are strictly similar to literature data,[14] this is in line with a low vanadium content in the zircon structure and with the high concentration of leached vanadium (value discussed in the Section 3.6). The QPA of ZV530 revealed the presence of ZrO_2 as main crystal phase, NaCl and LiF; the amorphous phase was as high as 37.0 wt.%; the colour parameters were typical of yellow species. QPA of ZV730 and ZV930 indicated that $ZrSiO_4$ was the main phase (64.0 and 79.0 wt.%), ZrO_2 and the amorphous amount decreased to 22.0 and 6.5 wt.%, respectively; the best data fitting was reached by taking into consideration also $Li_2Si_2O_5$ and $Na_{0.7}V_6O_{15}$. The colour parameter of ZV series fall in a very narrow range $61 \le L^* \le 69$, $-16 \le a^* \le -15$, $-25 \le b^* \le -24$ except for ZV930 who has no good a^* and b^* parameters. So it seems that the temperature range for a high $ZrSiO_4$ yield and good blue colour is $730 < T < 930$ °C. On the basis of the
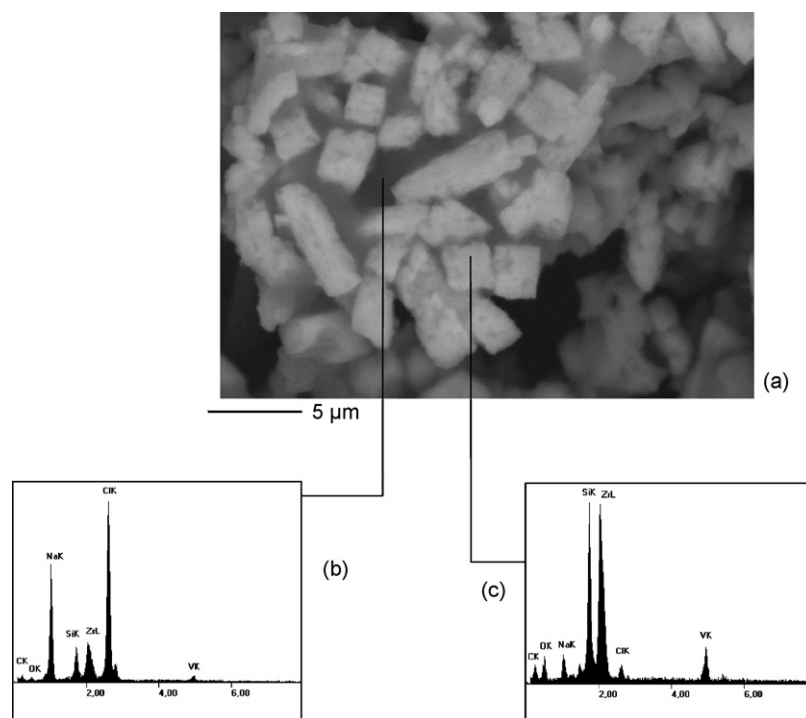

Fig. 1. SEM micrographs (4000×) and correspondent EDS spectra of sample ZV4uw (a–c).

results from HT-XRD and QPA, we can propose that up to 530 °C the thermal decomposition of Zr(IV)- and V(IV)–citrate and LiNO$_3$ is the main process and it is accompanied by the crystallization of ZrO$_2$, LiF and NaCl. At temperature lower than 730 °C LiF starts to react with silica forming volatile species such as SiF$_4$, that afterwards reacts with amorphous ZrO$_2$ to form ZrSiO$_4$, while lithium forms lithium disilicate; the increase of temperature allows also the reaction of lithium silicates with ZrO$_2$ to form ZrSiO$_4$ and the chloride ion reacts with lithium forming LiCl. The temperature increase favours also the vanadium (IV) oxidation to vanadium (V) so disfavouring a great V(IV) incorporation in to the ZrSiO$_4$ structure. The development of blue colour required that ZrSiO$_4$ synthesis and vanadium incorporation into ZrSiO$_4$ structure occurred simultaneously. The colour parameters become better at increasing temperature and the best values were calculated in the range 730–930 °C, in the same interval ZrSiO$_4$ becomes the first phase.

3.6. Leaching of the final product

The sample ZV4 was washed either with boiling water or with 0.3 mol/L HNO$_3$. The concentration of leached sodium (127 and 129 ppm for water and acid, respectively), vanadium (59 and 57 ppm for water and acid, respectively), zirconium (5 and 3 ppm for water and acid, respectively), lithium (4 ppm in both cases) and silicon (>1 ppm in both cases) was strictly similar in both cases. It was worth nothing the amount of released vanadium indicating that its incorporation in the ZrSiO$_4$ structure has been moderate.

3.7. Morphological and compositional study by SEM/EDS

The sample ZV4 unwashed (Fig. 1a) showed light regular aggregates in a dark amorphous matrix that contained essentially Na and Cl (Fig. 1b) and as minor constituents Zr, Si, O and V; the aggregates (Fig. 1c) contained Si, Zr, V, Na, O, Cl (ordered following the decreasing atomic abundance) with a Si/Zr atomic ratio (calculated by peak areas) ≅ 1.2. For sample ZV60 the matrix morphology changed and its composition became poorer of Na and Cl. The EDS analyses did not reveal the presence of fluoride ion, similarly to the absence of NaF in all XRD spectra, this could be due to its consumption during the heating cycle.
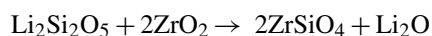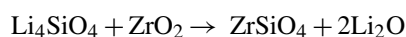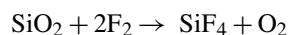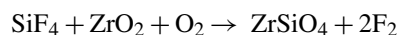
3.8. Enamelling of pigment

The colour parameters of ZV4 were almost unaffected by the addition to the glaze and by the thermal treatment, indicating that the blue colour at 900 °C was stable. The colour parameters of commercial pigment were greatly improved after the enamelling process and the comparison between commercial and ZV4 washed showed better results for the commercial one.

On the basis of present and literature results[19] we can propose these reactions for ZrSiO$_4$ synthesis in our experimental conditions:

- $530 < T°C < 730$

$$4LiF + SiO_{2\,amorphous} \rightarrow SiF_4 + 2Li_2O$$

$$2Li_2O + 4SiO_{2\,amorphous} \rightarrow 2Li_2Si_2O_5$$

$$2Li_2O + SiO_{2\,amorphous} \rightarrow Li_4SiO_4$$

- $730 < T°C < 930$

$$SiF_4 + ZrO_2 + O_2 \rightarrow ZrSiO_4 + 2F_2$$

$$SiO_2 + 2F_2 \rightarrow SiF_4 + O_2$$

$$Li_4SiO_4 + ZrO_2 \rightarrow ZrSiO_4 + 2Li_2O$$

$$Li_2Si_2O_5 + 2ZrO_2 \rightarrow 2ZrSiO_4 + Li_2O$$

4. Conclusions

The synthesis of V–ZrSiO$_4$ starting from an aqueous solution showed that:

- at temperature as low as 800 °C with an overall thermal cycle of 3 h and composition (ZrO$_2$)(SiO$_2$)(V$_2$O$_5$)$_{0.09}$, ZrSiO$_4$ is the main crystal phase (78.0 wt.%) and the colour parameters correspond to a good blue colour;
- the use of mineralizer in the composition (ZrO$_2$)(SiO$_2$)(NaF)$_{0.16}$(V$_2$O$_5$)$_{0.09}$(LiNO$_3$)$_{0.09}$, with thermal cycle 2 h long and $T_{max} = 800$ °C, gives rise to a 73.0 wt.% of ZrSiO$_4$ and good colour parameters; after washing and dissolution of soluble species the ZrSiO$_4$ yield increases to 85.0 wt.%;
- by using an overall thermal cycle 4 h long ($T_{max} = 730$ °C) it is possible to obtain both a good blue colour and a high ZrSiO$_4$ yield (64.0 wt.%);
- a fast thermal cycle gives better results than a slow one, because the former is characterized by a rate of parent oxides crystallization at low temperature which is reduced with respect to ZrSiO$_4$ one;
- vanadium can act as mineralizer and the ZrSiO$_4$ can be obtained without addition of further mineralizers;
- the addition of NaF does not favour ZrSiO$_4$ formation at low temperature;
- the addition of a moderate amount of LiNO$_3$ (0.09 mol) favours the ZrSiO$_4$ formation and the incorporation of vanadium in ZrSiO$_4$ structure at $T < 800$ °C. Fairly good blue colour was obtained and above this value the effect is reversed;
- the addition of a mixture of NaF and LiNO$_3$ improves colour parameters and ZrSiO$_4$ yield;
- after glazing (900 °C) the colour parameters are unchanged with respect to unglazed pigment.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jeurceramsoc.2006.05.063.

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