Dyes and Pigments 94 (2012) 207–211

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Agricultural waste in the synthesis of coral ceramic pigment

Fernanda Andreola, Luisa Barbieri, Federica Bondioli*

Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università di Modena e Reggio Emilia, Via Vignolese 905, 41125 Modena, Italy

ARTICLE INFO

Article history:
Received 20 September 2011
Received in revised form
8 January 2012
Accepted 11 January 2012
Available online 20 January 2012

Keywords:
Pigments
Zircon
Traditional ceramics
Rice husk ash
Pigment
Rice husk ash

ABSTRACT

This work reports the results of an evaluation of the use of rice husk ash as the source of silica in the preparation of coral ceramic pigments. $ZrSiO_4$–Fe_2O_3 inclusion pigments have been synthesized by solid state reactions evaluating the effect of the mineralizer and both silica and iron oxide precursors on the reactivity of the system. The colour developed in the derived ceramic glazes has been compared with the colour developed in comparative pigments prepared from pure SiO_2.

1. Introduction

Inorganic natural and synthetic pigments produced and marketed as fine powders are an integral part of many decorative and protective coatings and are used for the mass colouration of many materials, including glazes, ceramic bodies and porcelain enamels. In all these applications, pigments are dispersed in the media, forming a heterogeneous mixture. Therefore, powders used for colouring ceramics must show thermal and chemical stability at high temperature and must be inert to the action of molten glass (frits or sintering aids).

Considerable effort has been dedicated to the reduction of the cost of pigment production which in turn impacts upon the total price of a low added value product such as a ceramic tile. Different technological innovations, such as the rotative furnace, or different raw materials have been used. Furthermore, in this field wastes should be considered as resources that are already extracted and therefore usable [1]. Moreover, the recycling of material can be seen as a prevention of waste produced in the context of extracting raw materials responding both to an environmental and a technological demand.

The possibility to use industrial waste in the production of ceramic pigments has been evaluated by several authors, i.e. using metal-ions containing sludge [2], chromium-rich tannery waste [3] or titania-rich slag [4].

To the best knowledge of the author, however, Bondioli et al. has been the first that reported the use of agro-waste in this field in the synthesis of (Pr,Zr)SiO_4 yellow pigment [5]. Following our earlier study we examine herein the use rice husk ash (RHA), as silica precursor, in the synthesis of the Fe_2O_3–$ZrSiO_4$ inclusion pigment. The inclusion pigments present the following characteristics: (a) they are composed of two or more different insoluble crystalline structures; (b) their behaviour in the presence of glazes is like a unique chromatic unit from a pigmentation point of view: the colour is not developed by the introduction of a coloured ion into the matrix lattice or by the formation of a solid solution, but the crystals responsible for the colour are small coloured crystals occluded in the matrix during its sintering process. Among the systems developed [6–8] haematite included in zircon (DCMA 14-44-5), also known as "coral pink" pigment, is one of the zircon-based pigments, together with the vanadium zircon blue (V,Zr)SiO_4 and the praseodymium zircon yellow (Pr,Zr)SiO_4, market leader in high temperature applications for the whitewares industry. In the Fe_2O_3–$ZrSiO_4$ synthesis, both zircon formation and haematite coarsening must occur simultaneously in order to guarantee efficient occlusion of haematite [9]. In this sense, the control of the synthesis steps, the choice of the raw materials and the optimization of the calcination time and temperature, are fundamental to obtain a high colour yield.

---

* Corresponding author. Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università di Modena e Reggio Emilia, Via Vignolese 905/a, 41100 Modena, Italy. Tel.: +39 (0) 592056242; fax: +39 (0) 592056243.

E-mail address: federica.bondioli@unimore.it (F. Bondioli).

0143-7208/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2012.01.007

RHA is obtained by burning the rice husk, and in particular in plants where rice milling is performed with cogeneration or similar facilities or in plants for the production of parboiled rice. In general, the so obtained RHA is dumped as a waste. Globally, approximately 600 million tonnes of rice paddy is produced each year. Assuming a husk to paddy ratio of 20% [10], and an ash to husk ratio of 18% [11], the total global ash production could be as high as 21,000,000 tonnes per year.

RHA is a general term describing all types of ash produced from burning rice husks. In practice, the type of ash varies considerably according to the burning technique. The silica in the ash undergoes structural transformations depending on the conditions (time, temperature, etc.) of combustion [12]. At 550–800 °C amorphous ash is formed and at higher temperatures than this, crystalline ash is formed. These types of silica have different properties, the correct specifications of which are important to produce ash for the particular end use.

The presence of silica in RHA has been known since 1938 [13] and an extensive literature search has highlighted many uses of RHA as a silica replacement. Two main industrial uses have been identified: as an insulator in the steel industry and as a cement extender to Portland cement concrete mixture in the cement industry. RHA is used by the steel industry in the production of high quality flat steel. Moreover, RHA is an excellent insulator, having low thermal conductivity, high melting point, low bulk density and high porosity. It is this insulating property that makes it an excellent 'tundish powder' that prevents rapid cooling of the steel and ensures uniform solidification in the continuous casting process. On the other hand, substantial research has been carried out on its use in the manufacture of concrete. In particular, there are two areas for which RHA is used: in the manufacture of low cost building blocks, and in the production of high quality cement [14]. The addition of RHA to cement has been found to enhance cement properties [15]. In general, concrete made with Portland cement containing RHA has a higher compressive strength.

The use of RHA as a silica replacement in the ceramic field was studied in the laboratory by several authors. Prasad et al. [16,17] investigated the effect of rice husk ash in traditional whiteware compositions completely replacing the quartz phase without substantial modification to the physical and mechanical properties of the products. Naskar et al. investigated the possibility to use this agricultural waste material to synthesize lithium aluminium silicate (LAS) glass ceramics [18] and cordierite [19] while Wattanasiriwech et al. reported the use of RHA for quartz substitution in glazes making a choice of the model system soda-lime glass [20].

In this study, Fe_2O_3–$ZrSiO_4$ red/coral pigment has been synthesized by solid state reactions using RHA as a silica precursor as received from a parboiled industrial plant. In this field wastes should be examined as resources that are already extracted and therefore usable and the recycling of material can be seen as a prevention of waste produced in the context of extracting raw materials. The obtained powders have been characterized mainly by X-ray diffraction and SEM analysis, and the colour developed in a suitable ceramic glaze has been investigated in comparison with the colour developed by the pigments prepared from pure SiO_2.

2. Experimental procedures

The pigments have been produced by calcining a mixture of monoclinic zirconia (ZrO_2) and silica precursor (both RHA and commercial quartz), carefully weighted following the stoichiometry of zircon ($ZrSiO_4$), together with the colouring precursor and mineralizers (NaX, where X = Cl, F). To evaluate the effect of different haematite precursors on the final colour of the powders, both α-Fe_2O_3 and FeOOH have been used. To reproduce the industrial pigment formation, all the raw materials have been used as received without any purification or grinding.

The batches have been prepared taking into account chemical composition (ICP spectroscopy, Liberty 200, Varian and Elemental Analysis, mod. 1110, Carlo Erba) of the agricultural waste (Table 1) kindly supplied by Riso Flora S.p.A. (Italy). The complete RHA characterization is reported elsewhere [21].

Appropriately weighed raw materials have been dry mixed for 30 min to obtain a pigment containing 15 wt% of Fe_2O_3. In some samples 6 wt% of NaCl and 4 wt% of NaF have been added as mineralizers. In Table 2 all the prepared mixtures have been reported together with the used codification.

The thermal behaviour of raw materials has been studied using a simultaneous thermogravimetric and differential thermal analyser (TG-DTA, mod. 409, Netzsch). About 30 mg of powdered sample, <25 μm in grain size, has been subjected to a thermal treatment from 20 to 1400 °C at a heating rate of 10 °C/min.

The mixtures have been calcined in closed porcelain crucibles at different temperatures (800–1200 °C range) at a heating rate of 10 °C/min for 60 min of soaking time and then wet milled up to chloride elimination. In order to determine the crystalline phases present on the calcined powdered samples, X-ray diffraction measurements (XRD) have been carried out using a conventional Bragg-Brentano diffractometer (PW 3710, Philips Research Laboratories) with Ni-filtered CuKα radiation. The morphology of the obtained pigments has been examined by scanning electron microscopy (SEM, Model XL40, Philips Research Laboratories) equipped with an energy dispersion spectroscopy equipment (EDAX, Philips Research Laboratories).

Finally, the powders calcined at 1000 °C have been tested as pigments for glaze colouring. Two ceramic frits for high temperature, a glossy (A) and a white glossy (B) composition (Table 1), have been used for pigment application. The pigments, added to the composition at 3 wt%, have been wet mixed with the ceramic frit for 30 min in a blender-mixer and then dried. The slips were deposited on ceramic tile supports by a scalpel obtaining a uniform glaze layer and then fired in an industrial high speed roller kiln using a typical industrial cycle of ≈45 min with a maximum temperature of 1180 °C.

Colour measurements have been performed on both pigments and glazes by UV–Vis spectroscopy (model Lambda 19, Perkin Elmer) using the CIELab method in order to obtain L^*, a^* and b^* values.

3. Results and discussion

The chemical analysis of the rice husk ash used is reported in Table 1. The obtained data confirmed that the RHA, although containing 8 wt% of unburned carbon, is a waste that contains 80 wt% of very pure silica. In particular, the quantitative mineralogical analysis showed that RHA is mainly composed by amorphous silica (85.7(2) wt%) and cristobalite (11.5(1) wt%) and tridymite (2.8(2) wt%) as crystalline phases [21]. Other oxides are all lower than 1.5 wt%; the chromophore oxides, in particular Fe_2O_3 e TiO_2 that can

Table 1
Chemical analysis of the rice husk ash (RHA) and chemical compositions of the frits.

Oxide	RHA (wt%)	Frit A (wt%)	Frit B (wt%)	Oxide	RHA (wt%)	Frit A (wt%)	Frit B (wt%)
SiO_2	81.09	67.83	66.96	K_2O	1.39	2.80	2.21
Al_2O_3	0.05	4.69	3.05	ZnO	0.01	8.41	11.81
Fe_2O_3	0.14	0.08	0.09	MnO	0.14	/	/
TiO_2	0.03	0.02	0.02	SO_3	1.45	/	/
CaO	1.07	15.66	6.87	P_2O_5	3.23	/	/
MgO	0.75	0.51	3.20	ZrO_2	/	/	5.76
Na_2O	/	/	0.03	L.O.I.	8.73	/	/

Table 2
Precursors used to prepare the different batches.

Code	Raw materials				
E0	Fe_2O_3	Quartz	ZrO_2	NaCl	NaF
E1	Fe_2O_3	Quartz	ZrO_2	/	/
G0	FeOOH	Quartz	ZrO_2	NaCl	NaF
G1	FeOOH	Quartz	ZrO_2	/	/
E2	Fe_2O_3	RHA	ZrO_2	NaCl	NaF
E3	Fe_2O_3	RHA	ZrO_2	/	/
G2	FeOOH	RHA	ZrO_2	NaCl	NaF
G3	FeOOH	RHA	ZrO_2	/	/

influence the colour developed by the pigment in a ceramic matrix, are present only as traces. Taking into account the different raw materials chemical analysis, eight different batches (Table 2) have been obtained and characterized by thermal analysis.

In Fig. 1 the TG-DTA curve of the mixture E0 is reported as representative of all batches prepared using quartz as the silica precursor. Moreover, in Fig. 2 the XRD patterns of the sample calcined at different temperatures are reported. The combined analysis of the thermal and mineralogical analysis allows better evaluation of the thermal behaviour of the mixture. In particular after the endothermal transformation α to β quartz at 580 °C, the endothermal event at around 700 °C, not correlated to a weight loss, is due to the fusion of mineralizers present in the batch. This evidence underlines that in a first step mineralizers act in the liquid phase to enhance the synthesis rate of zircon governed by diffusion [22]. Below 1000 °C, quartz (ICDD# 01-083-0539), haematite (ICDD# 01-089-2810) and monoclinic zirconia (ICDD# 01-083-0942) are the main crystallographic phases (Fig. 2a) even if the relative quantity changes with temperature indicating a higher dissolution rate of silica in the liquid phase due the mineralizer presence. The weight loss of ≈5 wt% at around 1000 °C is due to the mineralizers evaporation indicating that at this temperature they operate in the vapour phase following a two-step mechanism [22]. Zircon phase (ICDD# 01-071-0991) crystallized at this temperature and can be distinguished by XRD analysis only in the pattern of the mixture calcined at 1100 °C (Fig. 2b). At 1170 °C the endothermal event in the DTA curve is attributable to the monoclinic to tetragonal transformation of the residual unreacted zirconia.

In Fig. 3 the TG-DTA curve of the mixture E2 is reported as representative of all batches prepared using RHA as the silica source. Moreover, as already done for the E0 sample, in Fig. 4 the XRD patterns of the sample calcined at different temperature are reported. The curves are very similar to that obtained on E0 samples even if with some important thermal event characteristic of the silica precursor used. The exothermal event at around 500 °C, in fact, can be attributed to the combustion of unburned carbon present in the RHA waste. The weight loss of 4 wt%

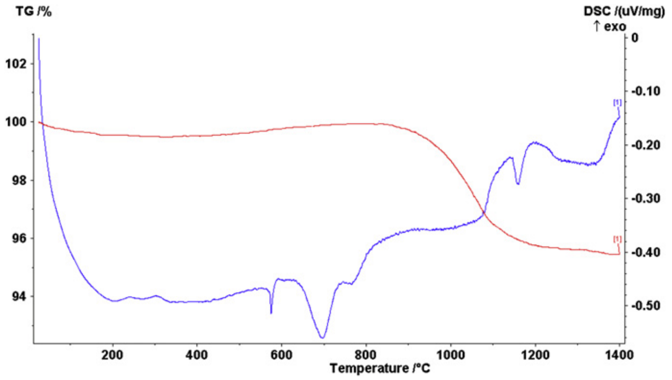

Fig. 1. TG-DTA curves of E0 mixture chosen as representative of all batches prepared using quartz as silica precursor.

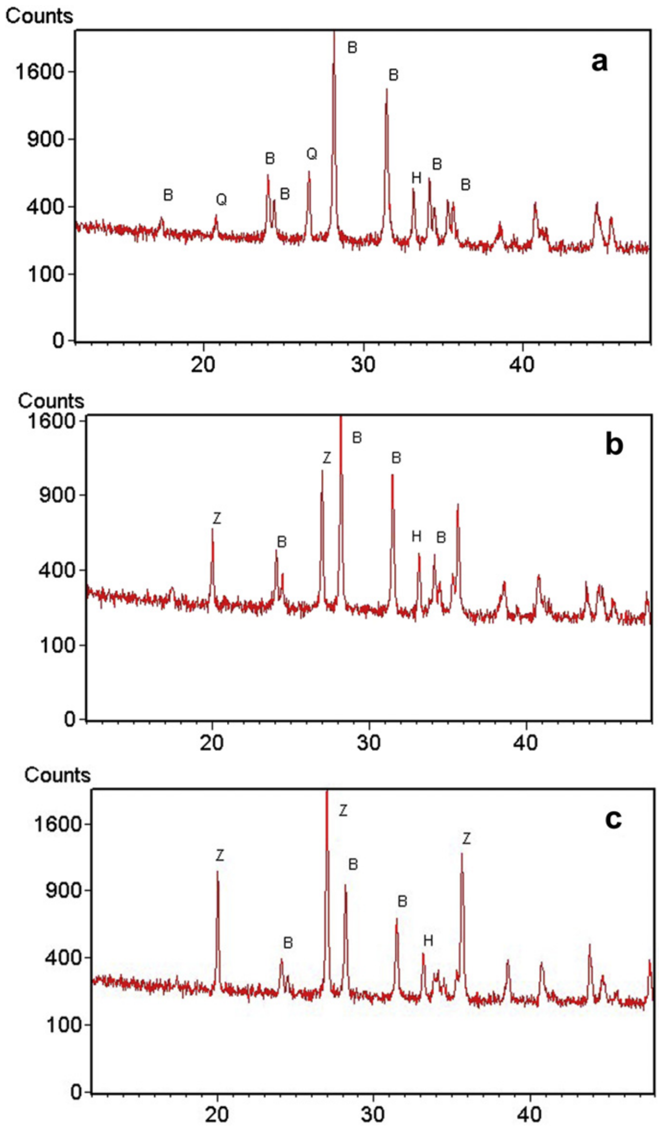

Fig. 2. XRD patterns of the E0 mixtures calcined at 1000 (a), 1100 (b) and 1200 °C (c). Z = $ZrSiO_4$; B = m-ZrO_2; Q = Quartz; H = Haematite.

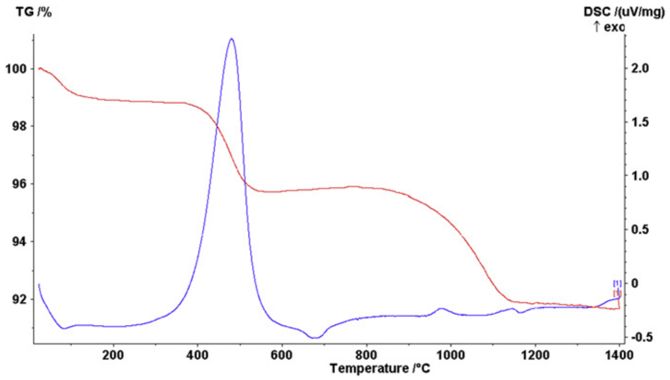

Fig. 3. TG-DTA curves of E2 mixture chosen as representative of all batches prepared using RHA as silica precursor.

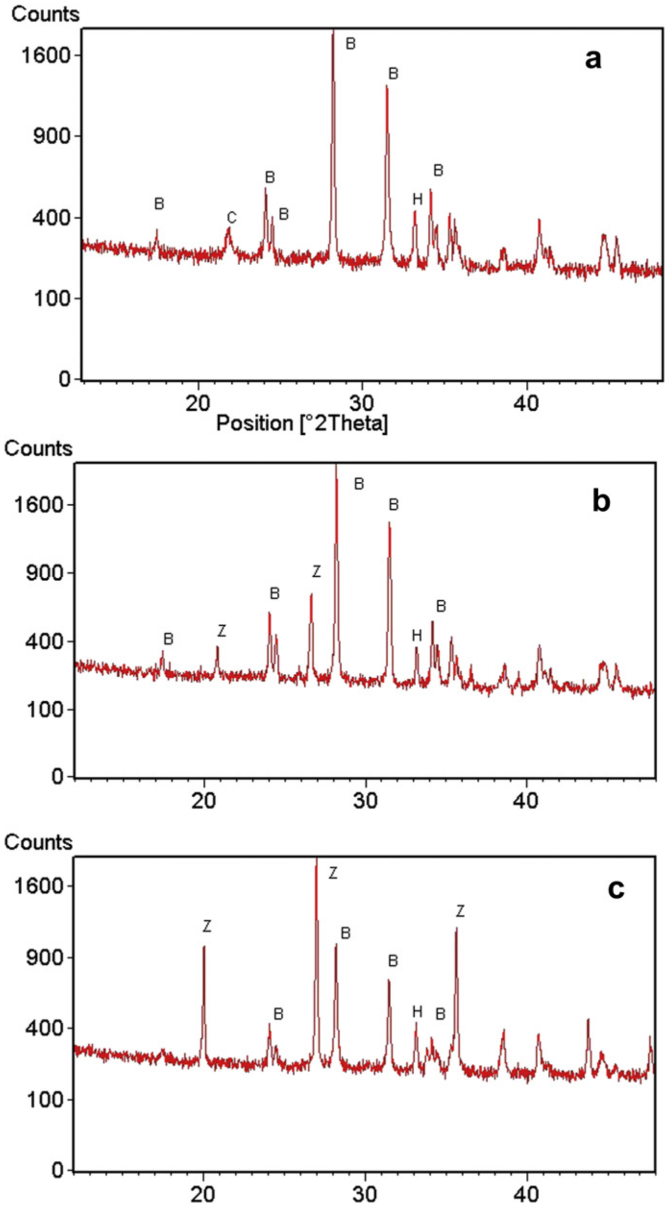

Fig. 4. XRD patterns of the E2 mixtures calcined at 800 (a), 1000 (b), and 1200 °C (d). Z = $ZrSiO_4$; B = m-ZrO_2; C = Cristobalite; H = Hematite.

associated to this reaction is in good agreement with the ash chemical analysis (Table 1) taking into account the mixture formula. Cristobalite (ICDD# 01-076-0940) instead of quartz is the silica phase present in the mixture (Fig. 4a) indicating the different reactivity of the silica precursors. The higher reactivity is, moreover, underlined by the presence of zircon in the pattern of the mixture calcined at 1000 °C (Fig. 4b), 100 °C below with respect to the E0 mixture.

In both cases, however, at higher temperature (Figs. 2 and 4c) the main crystalline phase is zircon ($ZrSiO_4$) and haematite though the characteristic peaks of the unreacted monoclinic zirconia and silica (quartz or cristobalite depending on the used silica source) raw materials are still present.

Finally it is important to note that only the batches obtained using mineralizers allow zircon formation, underlining the necessity to use NaCl and NaF to obtain the required structure. For this reason the mixtures E1, G1, E3 and G3 have not been further characterised.

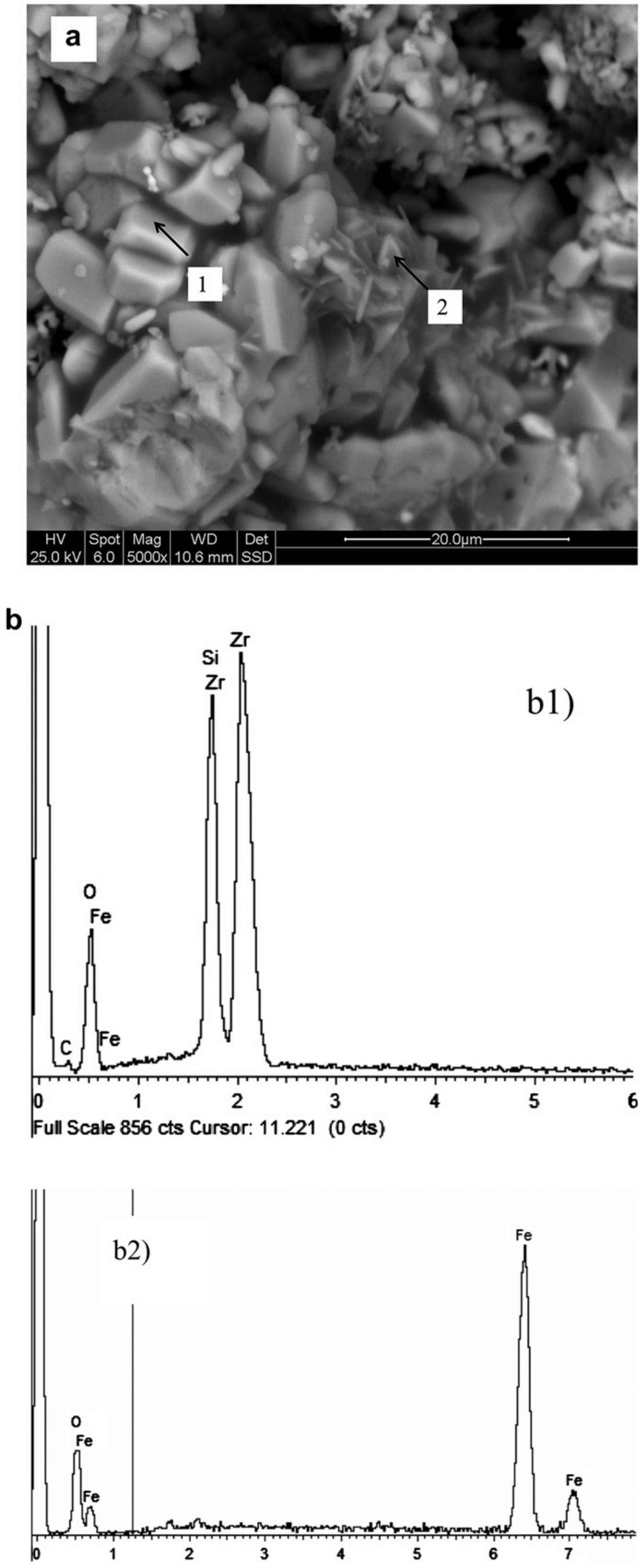

Fig. 5. SEM micrographs (a) and EDS spectra (b) of pigment obtained starting from ash at 1000 °C.

Table 3
CIELab values of pigments calcined at different temperatures.

Code	*L**	*a**	*b**	Code	*L**	*a**	*b**
E0_800	44.22	12.54	4.99	E2_800	40.87	12.00	4.18
E0_1000	46.15	10.87	4.80	E2_1000	44.46	7.95	3.95
E0_1100	47.58	9.23	4.31	E2_1100	44.32	7.53	3.64
E0_1200	49.67	7.12	3.69	E2_1200	46.82	7.62	3.48
G0_800	45.22	12.87	4.23	G2_800	42.31	11.63	4.84
G0_1000	45.56	12.65	4.34	G2_1000	42.38	8.56	4.72
G0_1100	48.35	11.76	3.85	G2_1100	43.58	8.49	3.92
G0_1200	49.18	10.84	3.62	G2_1200	44.87	7.92	3.06

Table 4
CIELab values of glazes obtained with pigments calcined at 1000 °C and frit A and B respectively.

Code	*L**	*a**	*b**	Code	*L**	*a**	*b**
E0_A	79.19	4.25	14.71	E2_A	78.63	5.96	13.53
E0_B	83.56	3.44	7.47	E2_B	81.87	3.98	8.60
G0_A	81.67	3.39	12.21	G2_A	80.44	3.86	12.67
G0_B	81.56	2.6	9.59	G2_B	84.10	2.87	7.39

The SEM and EDS analysis (Fig. 5a and b), independently on the silica precursor used, evidenced the formation of rhombohedrical crystals of zircon with a homogenous and narrow grain size distribution centred at around 10 μm. Moreover, in accordance with XRD patterns, acicular crystals of Fe_2O_3 are visible due to the nature of the heteromorphic pigment.

In Table 3, the CIElab values of the calcined powders are reported. In particular, the a^* parameter, that indicates the predominance of the red colour (positive values) on the green colour (negative values), is for this pigment the most representative value. The table shows that the a^* parameter, independently to the silica and iron oxide precursors, decreases as the temperature of pigment calcination is increased. It could be hypothesized that for the pigments, the calcination temperature directly influences the inclusion efficiency. The a^* parameter decreases when free haematite is included in the zircon matrix that crystallizes during the calcination step.

The colour developed by the different precursors is quite the same even if the a^* value is always higher for the samples obtained starting from the commercial quartz especially if prepared with FeOOH (G0 samples).

However the successful formation of the Fe_2O_3–$ZrSiO_4$ inclusion pigment has to be confirmed by a glaze colouring test. The powders calcined at 1000 °C have been used as pigments for glaze colouring to define their thermal and chemical stability in two different ceramic glazes (Table 1). In Table 4 the CIElab values of the obtained glazes are reported. Irrespective of the raw materials used, the Table shows that the obtained pigments develop a good red colour indicating the chemical and thermal stability of the synthesized powder pigments. In particular, in both the utilised glazes, the pigments obtained starting from RHA seem to develop a better red colour. In fact the a^* parameter of glazes coloured by pigments obtained with RHA (E2 and G2 samples) is higher than that obtained with commercial quartz (E0 and G0 samples) with an opposite behaviour with respect of the pigment colour. It could be hypothesized that for the pigments the silica source directly influences the inclusion efficiency. In fact using RHA, haematite particles would be more efficiently included (probably due to the different rate of zircon crystallization and sintering) and thus more efficiently protected by zircon grains against the action of molten glass during the enamel firing, allowing to a higher cromophore efficiency.

4. Conclusion

This work allows us to confirm the possibility of using rice husk ash as a silica precursor for the development of ceramic pigments. The characterization carried out corroborates the thermal and chemical stability of the synthesized coral pigment. The obtained pigments are stable and develop, in commercial glazes, an interesting red colour that is more intense with respect to the colour developed by the pigments obtained starting from pure quartz.

Acknowledgement

The authors thank Ing. Luca Bertacci for his support to the experimental procedure. Dr. Marcaccioli, BONET Group (I), is gratefully acknowledged for the furnished materials and for his constant support to evaluate the ceramic applicability.

References

[1] Andreola F, Barbieri L, Bondioli F, Cannio M, Ferrari AM, Lancellotti I. Synthesis of chromium containing pigments from chromium galvanic sludges. J Hazard Mater 2008;156(1–3):466–71.
[2] Labrincha JA, Hajjaji W, Seabra MP. Evaluation of metal-ions containing sludges in the preparation of black inorganic pigments. J Hazard Mater 2011; 185(2–3):619–25.
[3] Toffoli SM, Abreu MA. Characterization of a chromium-rich tannery waste and its potential use in ceramics. Ceram Int 2009;35(6):2225–34.
[4] Sahu KK, Alex TC, Mishra D, Agrawal A. An overview on the production of pigment grade titania from titania-rich slag. Waste Manage Res 2006;24(1): 74–9.
[5] Bondioli F, Andreola F, Barbieri L, Manfredini T, Ferrari AM. Effect of rice husk ash (RHA) in the synthesis of (Pr, Zr)SiO_4 ceramic pigment. J Eur Ceram Soc 2007;27(12):3483–8.
[6] Hosseini-Zori A, Bondioli F, Manfredini T, Taheri-Nassaj E. Effect of synthesis parameters on a hematite-silica red pigment obtained using a coprecipitation route. Dyes Pigments 2008;77(1):53–8.
[7] Bondioli F, Manfredini T, Siligardi C, Ferrari AM. New glass-ceramic inclusion pigment. J Am Ceram Soc 2005;88(4):1070–1.
[8] Bondioli F, Ferrari AM, Leonelli C, Manfredini T. Syntheses of Fe_2O_3/silica red inorganic inclusion pigments for ceramic applications. Mater Res Bull 1998; 33(5):723–9.
[9] Llusar M, Badenes JA, Calbo J, Tena MA, Monros G. Analysis of the effect of different mineralizers in the ceramic synthesis of the "pink coral" iron-zircon pigment. Boletin De La Sociedad Espanola De Ceramica Y Vidrio 1999;38(3): 201–8.
[10] Beagle EC. Rice husk conversion to energy. FAO Agricultural Services Bulletin 1978;(I) [Rome].
[11] Velupillai L, Mahin DB, Warshaw JW, Wailes EJ. A study of the market for rice husk-to-energy systems and equipment. Louisiana State University; 1997.
[12] Bharadwaj A, Wang Y, Sridhar S, Arunachalam VS. Pyrolysis of rice husk. Curr Sci 2004;87(7):981–6.
[13] Martin JL. The densification of rice hulls and a study of the products obtained. Eunice. LA (USA): Louisiana State University; 1938.
[14] de Sensale GR. Effect of rice-husk ash on durability of cementitious materials. Cement Concrete Comp 2010;32(9):718–25.
[15] Chao-Lung H, Bui LAT, Chun-Tsun C. Effect of rice husk ash on the strength and durability characteristics of concrete. Constr Build Mater 2011;25(9): 3768–72.
[16] Prasad CS, Maiti KN, Venugopal R. Effect of rice husk ash in whiteware compositions. Ceram Int 2001;27(6):629–35.
[17] Prasad CS, Maiti KN, Venugopal R. Effect of substitution of quartz by rice husk ash and silica fume on the properties of whiteware compositions. Ceram Int 2003;29(8):907–14.
[18] Naskar MK, Chatteljee M. A novel process for the synthesis of lithium aluminum silicate powders from rice husk ash and other water-based precursor materials. Mater Lett 2005;59(8–9):998–1003.
[19] Naskar MK, Chatterjee M. A novel process for the synthesis of cordierite ($Mg_2Al_4Si_5O_{18}$) powders from rice husk ash and other sources of silica and their comparative study. J Euro Ceram Soc 2004;24(13):3499–508.
[20] Wattanasiriwech D, Polpuak N, Danthaisong P, Wattanasiriwech S. Use of rice husk ash for quartz substitution in stoneware glazes. J Sci Ind Res 2008;67(6): 455–60.
[21] Bondioli F, Barbieri L, Ferrari AM, Manfredini T. Characterization of rice husk ash and its recycling as quartz substitute for the production of ceramic glazes. J Am Ceram Soc 2010;93(1):121–6.
[22] Bondioli F, Corradi AB, Ferrari AM, Manfredini T, Baldi G. Environmental scanning electron microscopy (ESEM) investigation of the reaction mechanism in praseodymium-doped zircon. J Am Ceram Soc 2000;83(6):1518–20.