

# Effect of rice husk ash (RHA) in the synthesis of (Pr,Zr)SiO<sub>4</sub> ceramic pigment

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## Abstract

In this work the screening results of the scientific activity conducted on the possibility to use rice husk ash as silica precursor for ceramic pigments are reported. Ceramic pigments were synthesized by solid-state reactions and the color developed in a suitable ceramic glaze was investigated in comparison with the color developed by the pigments prepared from pure SiO<sub>2</sub>.

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## 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 coloration of many materials, including glazes, ceramic bodies and porcelain enamels. In all these applications, pigments are dispersed (they do not dissolve) in the media, forming a heterogeneous mixture. Therefore, powders used for coloring ceramics must show thermal and chemical stability at high temperature and must be inert to the action of molten glass (frits or sintering aids).

These requirements limit ceramic pigments to a very small number of refractory systems which are fully reacted and relatively inert to the matrix in which they are dispersed.<sup>1</sup> For these reasons zircon (ZrSiO<sub>4</sub>) based pigments are market leaders in the high temperature color range because of the high tinctorial strength and superior chemical stability during firing of this matrix.<sup>2</sup> Examples include the solid solutions turquoise blue and praseodymium yellow pigments,<sup>3</sup> in which dopant ions are, respectively, vanadium and praseodymium, and the inclusion coral pink pigment (hematite included in zircon crystals).<sup>4</sup>

Considerable efforts are being taken worldwide to minimize the cost of the pigments that are very incident on the total price of a low added value product as the ceramic tile. Different technological innovations, such as the rotative furnace, or different raw materials have been used. Furthermore, in this field wastes should be looked as resources that are already extracted and therefore usable.<sup>5,6</sup> Moreover, the recycling of material can be seen as a prevention of waste produced in the context of extracting raw materials.

The present study involves the synthesis of (Pr,Zr)SiO<sub>4</sub> yellow pigment<sup>7–14</sup> to evaluate the possibility to use rice husk ash (RHA), an agricultural waste, as silica precursor. This pigment, in fact, is normally produced by calcining a mixture of monoclinic zirconia (ZrO<sub>2</sub>) and silica (SiO<sub>2</sub>) in the stoichiometry of zircon, together with the coloring ion precursor (Pr<sub>6</sub>O<sub>11</sub>) and one or more mineralizers, i.e. NaF, NaCl or MgCl<sub>2</sub>.

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 RHA so obtained 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%,<sup>15</sup> and a ash to husk ratio of 18%,<sup>16</sup> 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,

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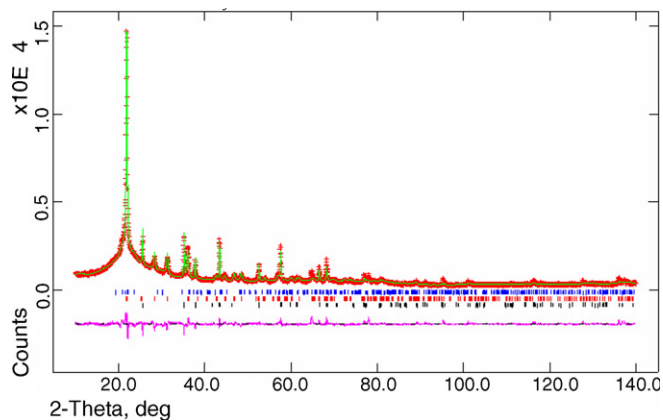


Fig. 1. Observed (crosses), calculated (continuous line) and difference curve from the Rietveld-R.I.R. refinement of the RHA sample. Markers representing the phase reflections correspond to corundum, tridymite and cristobalite low (from bottom to top).

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.<sup>17–19</sup> 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<sup>20</sup> and an extensive literature search has highlighted many uses of RHA as silica replacement. Two main industrial uses have been identified: as an insulator in the steel industry and as a pozzolan 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. The addition of

RHA to cement has been found to enhance cement properties. In general, concrete made with Portland cement containing RHA has a higher compressive strength.

The use of RHA in the form of silica in the ceramic field has been studied at a laboratory level by several authors. Prasad et al.<sup>21,22</sup> 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 and Chatterjee investigated the possibility to use this agricultural waste material to synthesize lithium aluminium silicate (LAS) glass ceramics<sup>23</sup> and cordierite.<sup>24</sup>

In this study, (Pr,Zr)SiO<sub>4</sub> yellow pigments have been synthesized by solid-state reactions using RHA as silica precursor as received by a preboiled industrial plant. The obtained powders have been characterized mainly by X-ray diffraction and SEM analysis, and the color developed in a suitable ceramic glaze has been investigated in comparison with the color developed by the pigments prepared from pure SiO<sub>2</sub>.

## 2. Experimental procedures

In order to evaluate the possibility to directly use rice husk ash in the production of ceramic pigments, the chemical (ICP Spectroscopy, Liberty 200, Varian and Elemental Analysis, mod. 1110, Carlo Erba) and mineralogical composition of the waste as obtained from the parboiled rice production, kindly supplied by Riso Flora S.p.A. (Italy), has been determined. Industrial quality monoclinic ZrO<sub>2</sub>, SiO<sub>2</sub> ( $\alpha$ -quartz), and Pr<sub>6</sub>O<sub>11</sub>, as well as mineralizers (NaX, where X = Cl, F), have been selected as raw materials for the pigment preparation. Thermal behaviour of raw materials has been studied using a simultaneous thermogravimetric and differential thermal analyzer (TG-DTA, mod. 409, Netzsch). About 30 mg of powdered sample <25  $\mu$ m in grain size has been subjected to a thermal treatment from 20 to 1400 °C at a heating rate of 10 °C/min.

To reproduce the industrial pigment formation, all the raw materials have been used as received without any purification or grinding. Appropriately weighted raw materials have been dry mixed for 30 min. Three different samples have been prepared: two compositions starting with RHA and with 0 and 3.5 wt%

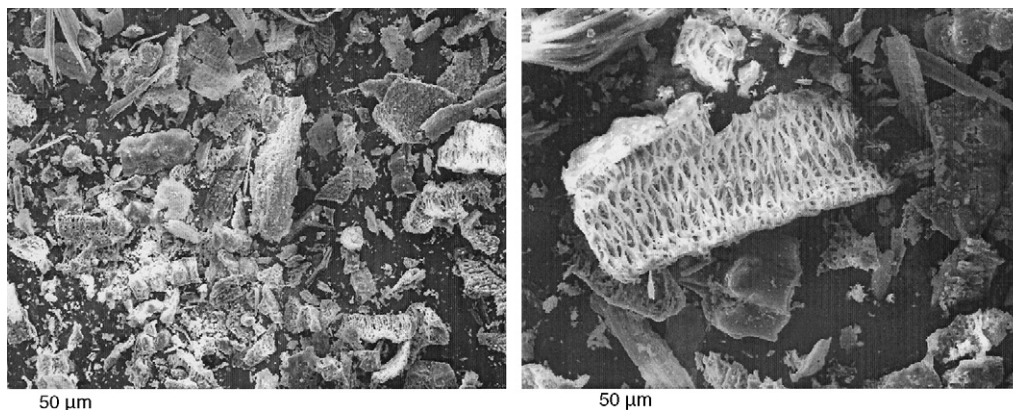


Fig. 2. SEM micrographs of the as received rice husk ash.

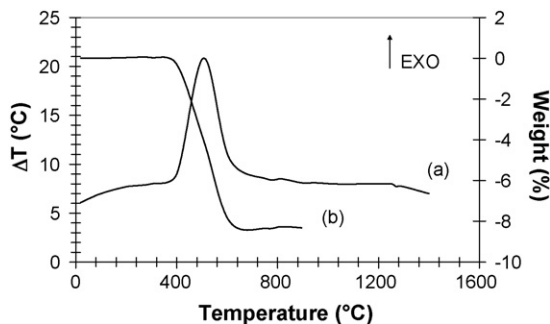


Fig. 3. DTA (a) and TG (b) curves of the as received rice husk ash.

of  $\text{Pr}_6\text{O}_{11}$ , respectively, and a composition starting from commercial silica and with 3.5 wt% of  $\text{Pr}_6\text{O}_{11}$ . This sample has been used as a reference in order to establish a comparison of the color strength with a traditional pigment composition. In all the prepared samples 4.5 wt% of NaF and 8 wt% of NaCl have been added as mineralizers. The so obtained mixtures have been calcined in a closed porcelain crucibles at different temperatures (950, 1050 and 1150 °C) for 60 min of soaking time and then wet milled. In order to qualitatively and quantitatively examine the crystalline phases present on the raw materials and 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 Cu  $K\alpha$  radiation. For the qualitative analysis the patterns have been recorded on the grounded samples (<25  $\mu\text{m}$  in size) in the 20–80°  $2\theta$  range at room temperature, with a scanning rate of 0.005°/s and a step size of 0.02°. For the quantitative analysis the combined Rietveld-Reference Intensity Ratio (R.I.R.) method has been used. A 10 wt% of corundum (NIST SRM 674a annealed at 1500 °C for 1 d to increase the crystallinity to 100 wt%) has been added to all samples as internal standard. The mixtures, ground in an agate mortar, have been side-loaded in an aluminum flat holder in order to minimize the preferred orientation problems. Data have been recorded in the 5–140°  $2\theta$  range (step size 0.02° and 6 s counting time for each step). The phase fractions extracted by the Rietveld-R.I.R. refinements, using GSAS software and EXPGUI as graphical interface,<sup>25,26</sup> have been rescaled on the basis of the absolute weight of corundum originally added to the mixtures as an internal standard, and therefore internally renormalized. The background has been successfully fitted with a Chebyshev function with a variable number of coefficients depending on its complexity. The peak profiles have been modeled using a pseudo-Voigt function with one Gaussian and one Lorentzian coefficient. Lattice constants, phase fractions and coefficients corresponding to sample displacement and asymmetry have been also refined.

The morphology and microstructure of the samples have been examined by scanning electron microscopy (SEM) (XL40, Philips Research Laboratories) equipped with an energy dispersion spectroscopy (EDS) equipment (EDAX, Philips Research Laboratories).

Finally, the obtained powders have been tested as pigments for glaze coloring. A ceramic glaze, having a typical composition

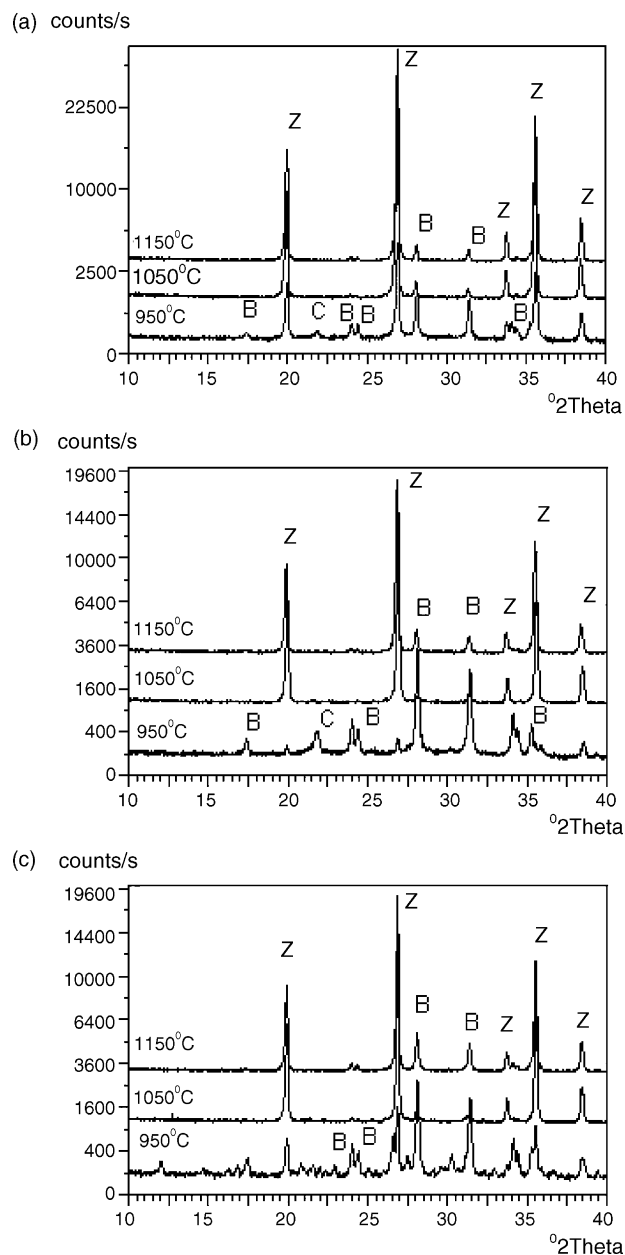


Fig. 4. XRD patterns of the calcined mixtures as a function of temperature: (a) rice husk ash and zirconia; (b) rice husk ash, zirconia and Pr oxide; (c) silica, zirconia and Pr oxide. Z =  $\text{ZrSiO}_4$ ; B =  $m\text{-ZrO}_2$ ; C = cristobalite.

for porcelainized stoneware (commonly known as gres porcelanato), has been used for pigment application. The pigments, added to the composition at 3 and 5 wt%, have been wet mixed with the ceramic frit for 30 min in a blender-mixer and then dried. The dried powders have been pressed at 40 MPa to produce wires (40 mm diameter) that have been fired in an industrial high-speed roller kiln using a typical industrial cycle of ~40 min with a maximum temperature of 1140 °C. Color 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

#### 3.1. Rice husk ash characterization

The chemical analysis of the rice husk ash used, as received by the parboiled plant of Riso Flora Italia, is reported in Table 1.

Regarding the loss of ignitions the elemental analysis defines that the hydrogen content is 0.15 wt%, the nitrogen content is 0.16 wt% while the carbon content is 8 wt% in accordance with the black color of the ash.

The chemical analysis, thus, confirms that the as received rice husk ash, though with 8 wt% of unburned carbon, is a waste that contains a 80 wt% of very pure silica. Other oxides are all lower than 1.5 wt%; the chromofore oxides, in particular  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ , that can influence the color developed by the pigment in a ceramic matrix, are present only as traces.

From a mineralogical point of view, Fig. 1 shows that RHA is mainly constituted by amorphous silica and, as crystalline phases, tridymite (JCPDF 18-1169) and cristobalite low (JCPDF 01-076-0935).

The quantitative analysis verifies this composition and highlights that the Rietveld-R.I.R method gives a deeper knowledge of the relative abundance of the crystalline phases. The results of the quantitative analysis of RHA are summarized in Table 2.

The quantitative results underline that, as reported by Ibrahim,<sup>27</sup> the thermal treatment performed on the rice to obtain the parboiled type favors the nucleation and growth of cristobalite phase which, in general, starts to appear at 900 °C.<sup>28</sup> The presence of tridymite, instead, is governed by the kind and amount of impurities.<sup>29</sup>

The microstructure analysis (SEM) of the RHA evidences that the as received powder is very coarse (Fig. 2); however, since it is easily crumbable, it was not necessary a further grinding before its mixing to the other raw materials. The EDS analysis, here not reported, confirmed the chemical analysis performed.

Table 1  
Chemical analysis of the rice husk ash used

Oxide	Composition (wt%)	Oxide	Composition (wt%)
$\text{SiO}_2$	81.09	$\text{K}_2\text{O}$	1.39
$\text{Al}_2\text{O}_3$	0.05	$\text{ZnO}$	0.01
$\text{Fe}_2\text{O}_3$	0.14	$\text{MnO}$	0.14
$\text{TiO}_2$	0.03	$\text{SO}_3$	1.45
$\text{CaO}$	1.07	$\text{P}_2\text{O}_5$	3.23
$\text{MgO}$	0.75	L.O.I.	8.73
$\text{Na}_2\text{O}$	–	TOT	98.08

Table 2  
Results of Rietveld-R.I.R. quantitative analysis (wt%) of RHA

Phases	Content (wt%)
Cristobalite low	17.2 (1)
Tridymite	5.6 (2)
Amorphous	77.2 (2)
Total	100.0
$\chi^2$	4.23
$R_{\text{wp}}$	0.077
$R_{\text{p}}$	0.057

Regarding the thermal behaviour, TG and DTA curves (Fig. 3) show an exothermal event at around 500 °C due to the combustion of unburned carbon present in the ash. In particular the weight loss associated to this reaction is around 8 wt% in good agreement with the chemical analysis results. Up to 1400 °C other thermal events are not evident.

#### 3.2. Pigments characterization

Fig. 4 reports the XRD patterns of the three mixtures calcined at 950, 1050 and 1150 °C.

The XRD patterns reported in Fig. 4a show the thermal evolution of the mixture obtained starting from ash without the chromofore oxide addition (0.0 wt%  $\text{Pr}_6\text{O}_{11}$  and mineralizers). In particular at 950 °C the main phase is already zircon ( $\text{ZrSiO}_4$ ) though the characteristic peaks of the unreacted monoclinic zirconia and cristobalite raw materials are still present. The XRD patterns reported in Fig. 4b show, instead, the thermal evolution of the colored mixture obtained starting from ash. At 950 °C the main phases are still monoclinic zirconia and cristobalite. Zircon and phases containing praseodymium are not present. At higher temperature it is possible to note the almost complete transformation of the raw materials in the desired product (with only small traces of unreacted monoclinic  $\text{ZrO}_2$ ). Finally, the XRD patterns reported in Fig. 4c show the thermal evolution of the colored mixture obtained starting from quartz. In comparison with the pigments obtained starting from ash a different reactivity is not visible being the phases present at the different temperatures the same and almost in the same ratio.

Regarding the formation of the  $(\text{Zr},\text{Pr})\text{SiO}_4$  solid solution, a shift of the (2, 0, 0) peak of zircon (to lower  $2\theta$  values) as the temperature is increased can be observed in Fig. 5a. This can be explained in terms of the increase of the distance between the planes of zircon in correspondence with the increasing Pr content in the structure, indicating an expansion of the elementary cell. This is by the way consistent with the substitution of  $\text{Pr}^{4+}$  ions for  $\text{Zr}^{4+}$  ions in the lattice (the ionic radii of  $\text{Pr}^{3+}$ ,  $\text{Pr}^{4+}$  and  $\text{Zr}^{4+}$  are 1.126, 0.90 and 0.72 Å, respectively, for eightfold coordination). A similar behaviour is also visible in the pigments obtained starting from quartz (Fig. 5b).

The SEM analysis (Fig. 6a and b), independently on the silica precursor used, evidenced the formation of rhombohedral crystals of zircon, starting from 1050 °C, with an homogenous and narrow grain size distribution centred at around 10 μm. Moreover, in accordance with XRD patterns, at 1150 °C the reaction is complete, and crystals of raw materials are not visible.

The successful formation of the pigmenting  $\text{Pr-ZrSiO}_4$  solid solution has been also confirmed by colorimetric analysis (Table 3). In fact, the  $b^*$  parameter, indicating the predominance of the yellow color ( $+b^*$ ) on the blue color ( $-b^*$ ), increases with the calcination temperature, irrespective of the silica precursor used. The color developed by the two precursor is quite the same and reach the higher yellowness at 1150 °C. For this reason only the pigments calcined at 1150 °C have been used to verify their chemical stability in a ceramic glaze. The color developed by these pigments added both at 3 and 5 wt% in an industrial glaze for high temperature is reported in Table 4. The table shows that

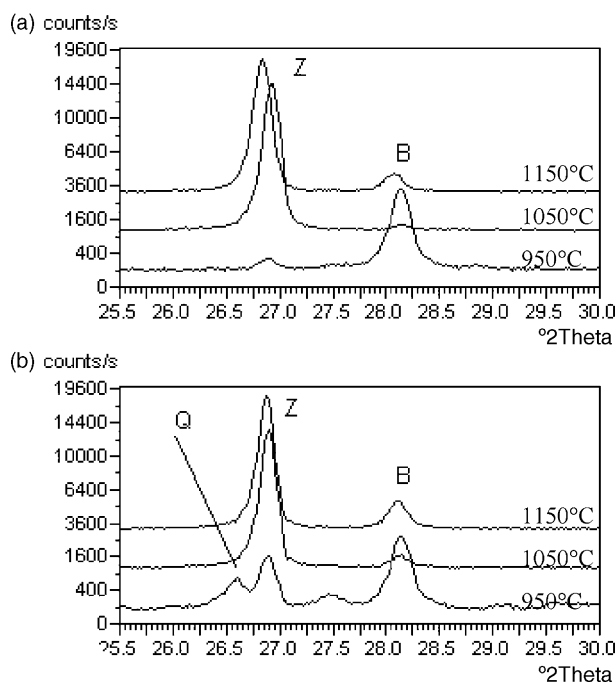


Fig. 5. XRD patterns as a function of temperature of pigments obtained starting from rice husk ash (a) and quartz (b). Z =  $\text{ZrSiO}_4$ ; B =  $m\text{-ZrO}_2$ ; Q = quartz.

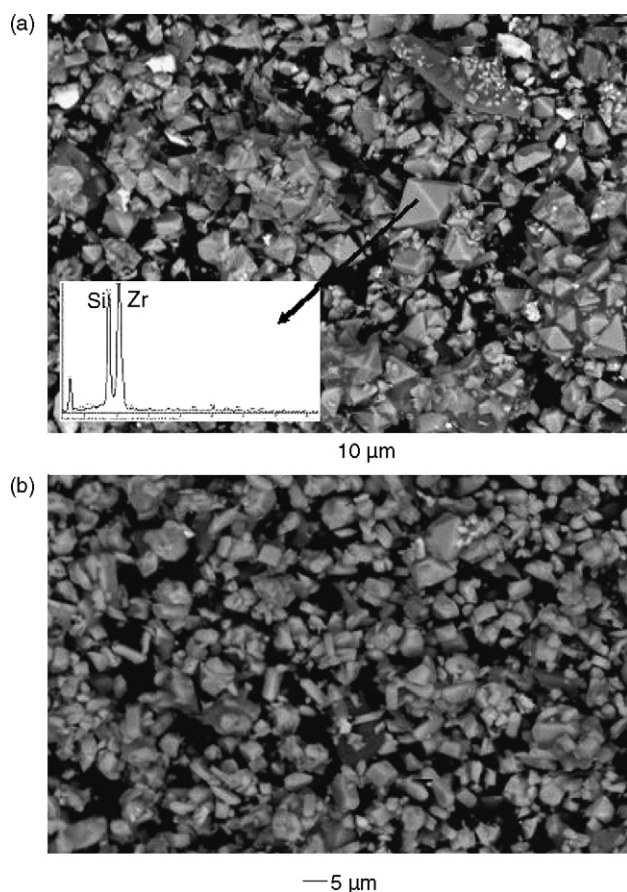


Fig. 6. SEM micrographs of the pigments obtained starting from ash at 1050 (a) and 1150 °C (b) (as representative).

Table 3

CIElab values of pigments obtained by ash and quartz as a function of temperature

Sample	$L^*$	$a^*$	$b^*$
Ash_950	76.01	-2.32	36.57
Ash_1050	79.94	-2.26	45.86
Ash_1150	77.00	5.13	58.12
Quartz_950	71.01	-2.21	42.57
Quartz_1050	76.94	-1.96	51.86
Quartz_1150	81.06	6.09	53.12

Table 4

CIElab values of the obtained glazes

Glaze	wt%	$L^*$	$a^*$	$b^*$
Ash_1150	3	83.72	-7.10	56.77
	5	83.79	-7.06	56.82
Quartz_1150	3	82.48	-7.86	52.50
	5	82.54	-7.92	52.41

the obtained pigments develop a good yellow color, irrespective of the raw materials used, indicating the chemical and thermal stability of the synthesized powders.

#### 4. Conclusion

This work allows us to confirm the possibility to use rice husk ash as silica precursor for the development of praseodymium doped zircon yellow pigment. The characterization carried out corroborates the thermal and chemical stability of the synthesized powders and allow us to determine the optimal synthesis conditions for the formation of the  $\text{Pr-ZrSiO}_4$  solid solution. The obtained pigments are stable and develop an intense yellow color that is very similar to the color developed by the pigments obtained starting from pure quartz.

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