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Ceramics International 34 (2008) 491–496

CERAMICS INTERNATIONAL

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# Effective factors on synthesis of the hematite–silica red inclusion pigment

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Received 7 March 2006; received in revised form 30 September 2006; accepted 24 November 2006

## Abstract

The work focuses on the synthesis of a red ceramic pigment by inclusion of hematite in a fumed silica matrix with different specific surface areas. Iron(II) sulfate was used as hematite precursor. Mixtures of iron(II) sulfate and fumed silica with different mole ratios were heated at different temperatures from 1000 to 1300 °C for 4 h.

Continuous changes in color were measured by comparing $L^*$–$a^*$–$b^*$ values of the heated samples. The fired pigments were enameled with a fritted glaze adding a 10 wt% of color in the glaze. The best red shades in the used glaze were obtained from samples heated at 1100–1200 °C for 4 h. Due to its chemical and thermal stability, the hematite/silica pigment may be considered as a suitable red pigment for ceramic manufacturing by fast firing cycles.

*Keywords:* Ceramic; Inclusion pigment; Non-toxic red pigment; Hematite–silica

## 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. In conclusion, 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. This need for great chemical and thermal stability has dominated research and development in recent years. In particular the interest is directed to the development of inclusion pigments which make utilizable coloring substances suffering the industrial thermal and chemical conditions by occluding them in a stable glassy or crystalline matrix (heteromorphic pigments) [1–12]. Among synthetic inorganic ceramic pigments, in fact, there is a restricted choice for red/pink and orange colors. These are generally easily etched by glasses, can be sensitive to the atmosphere and firing temperatures and a number of them contain toxic and pollutant elements. The inclusion or encapsulation of the reactive, colored or even toxic crystal into highly stable crystalline matrix gives a protection effect to the guest crystal by the host one.

Inclusion pigments present the following characteristics: (1) these contain two or more insoluble different crystalline phases; (2) their behavior in the presence of glazes is like a chromatic unit from a pigmentation point of view and the crystals responsible for the color are small colored crystals occluded during the sintering process of the matrix [3–5].

Amorphous silica may be considered to have a relatively low price giving it a potential to be used in occluded pigments as a matrix due to its properties and, in particular, to the sufficient thermal and chemical stability towards glassy phases. The high thermal stability of the silicon lattices and their properties such as sinterability at relatively low temperatures are well known [1,3].

Based on these considerations, the aim of the present work was to study the optimization of synthesizing red inorganic pigments for ceramic applications by conventional (thermal) inclusion of hematite ($\alpha$-$Fe_2O_3$) in a silica matrix starting from $FeSO_4 \cdot 7H_2O$ as iron oxide precursor.

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doi:10.1016/j.ceramint.2006.11.012

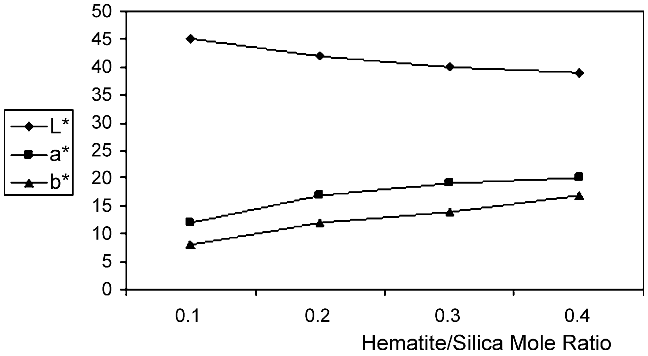

Fig. 1. Effect of $Fe_2O_3/SiO_2$ mole ratio on shade of powdered pigments containing fumed silica heated at 1200 °C for 4 h. Specific surface area was 255 $m^2/g$.

## 2. Experimental procedure

Pigments were prepared by conventional calcination in oxygen atmosphere in an electric tube furnace at 1000–1300 °C for 4 h (heating and cooling rate 20 °C/min) with mixtures of different compositions: $SiO_2$–$0.1Fe_2O_3$, $SiO_2$–$0.2Fe_2O_3$, $SiO_2$–$0.3Fe_2O_3$ and $SiO_2$–$0.4Fe_2O_3$ prepared by wet (acetone) homogenizations of iron(II) sulfate ($FeSO_4\cdot 7H_2O$; Merck Company) with amorphous fumed silica (Sigma Aldrich Company) having different surface areas: 200, 255 and 390 $m^2/g$.

The evolutions of crystalline phases in the calcined samples were studied by XRD using the conventional powder method. The XRD patterns were obtained by using an X'Pert diffractometer with Cu Kα radiation of a goniometer speed of 0.01° $2\theta$/s.

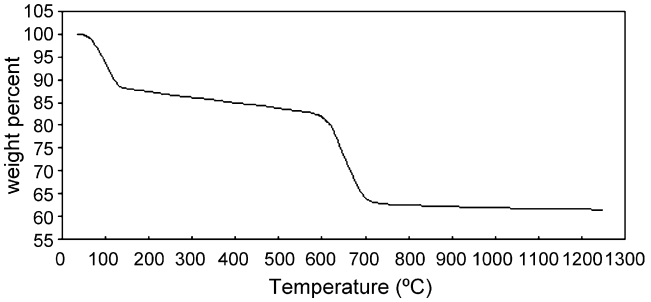

Fig. 2. TGA of the $SiO_2$–$0.2Fe_2O_3$ sample. Specific surface area was 255 $m^2/g$.

Table 1
Chemical analysis of the fritted glaze used by XRF and ICP (for indicating of $B_2O_3$)

| | |
|---|---|
| $SiO_2$ | 57.328 |
| $Al_2O_3$ | 6.815 |
| $Fe_2O_3$ | 0.226 |
| $Na_2O$ | 4.356 |
| $K_2O$ | 1.523 |
| CaO | 5.168 |
| MgO | 0.226 |
| $B_2O_3$ | 0.14 |
| Pb | 22.021 |
| Zn | 1.274 |
| Zr | 0.391 |
| Cl | 0.064 |

The effects of temperature of calcinations, composition (mole ratio of hematite/silica) and surface area of fumed silica on shade of the resulting red pigments were measured by a UV–vis spectrophotometer with analytical software for color

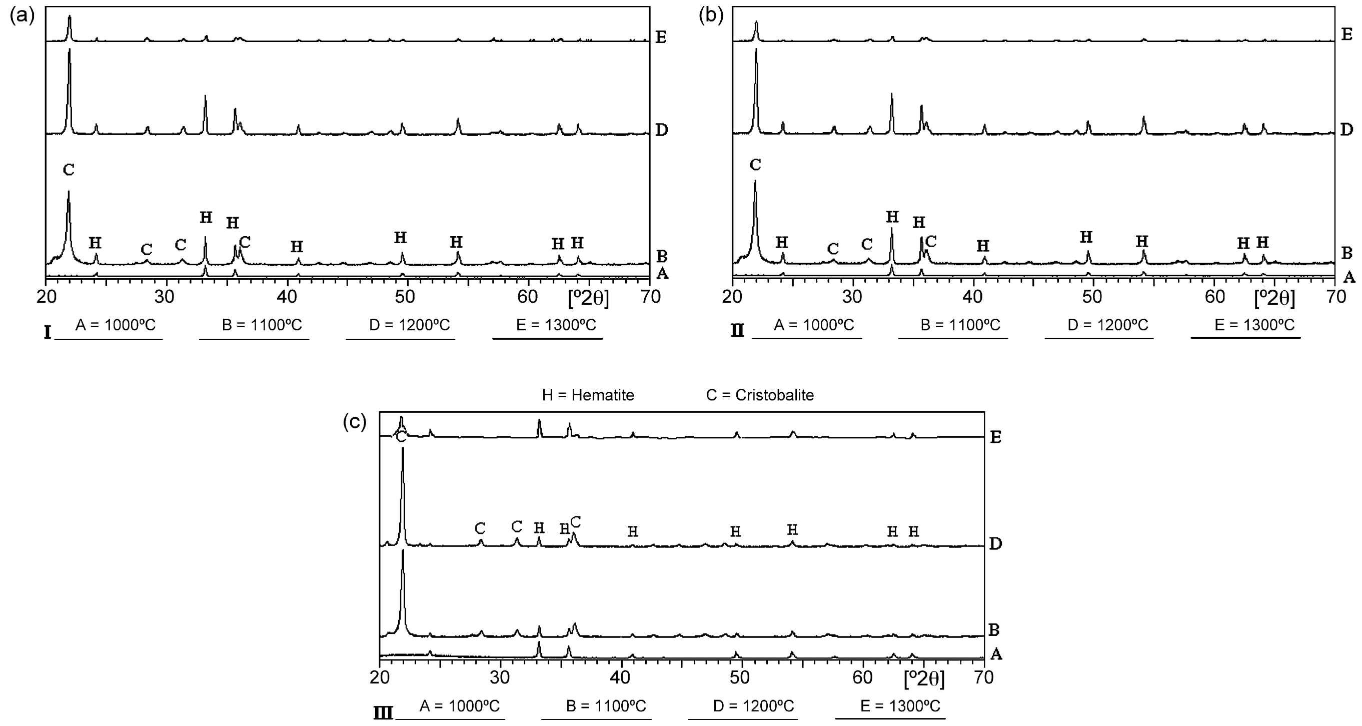

Fig. 3. Evolution of crystalline phases in the $SiO_2$–$0.2Fe_2O_3$ powdered pigments containing fumed silica with a specific surface area of (I) 200 $m^2/g$, (II) 255 $m^2/g$ and (III) 390 $m^2/g$ heated samples for 4 h at: (A) 1000 °C, (B) 1100 °C, (D) 1200 °C and (E) 1300 °C.

measurements (Gretag Macbeth$^{TM}$, Instrument: Color-Eye 7000, Observer: 10°). SEM observations were carried out by a Philips XL 40 scanning electron microscope.

The thermal behavior of the $SiO_2$–$0.2Fe_2O_3$ sample was studied by thermogravimetric analysis in air at a heating rate of 20 °C/min using a Netzsch TGA 409 equipment.

The fired pigments were enameled with a fritted glaze adding a 10 wt% of color in the glaze then fired at 1000 °C for 15 min. The composition of the fritted glaze is shown in Table 1. Finally a dry powdered sample of best red shade glaze was prepared only in an alumina cup and fired at mentioned condition. After normal cooling, the alumina cup was broken and some specimens of fired red glaze were powdered for XRD analysis. Reproducibility of best red shade in mentioned glaze was tested for three steps.

## 3. Results and discussion

In order to investigate the mole ratios of hematite/silica, different ratios from 0.1 to 0.4 were selected, primarily. Continuous changes in color were measured by comparing $L^*$–$a^*$–$b^*$ values of the heated samples. In ceramic practice the

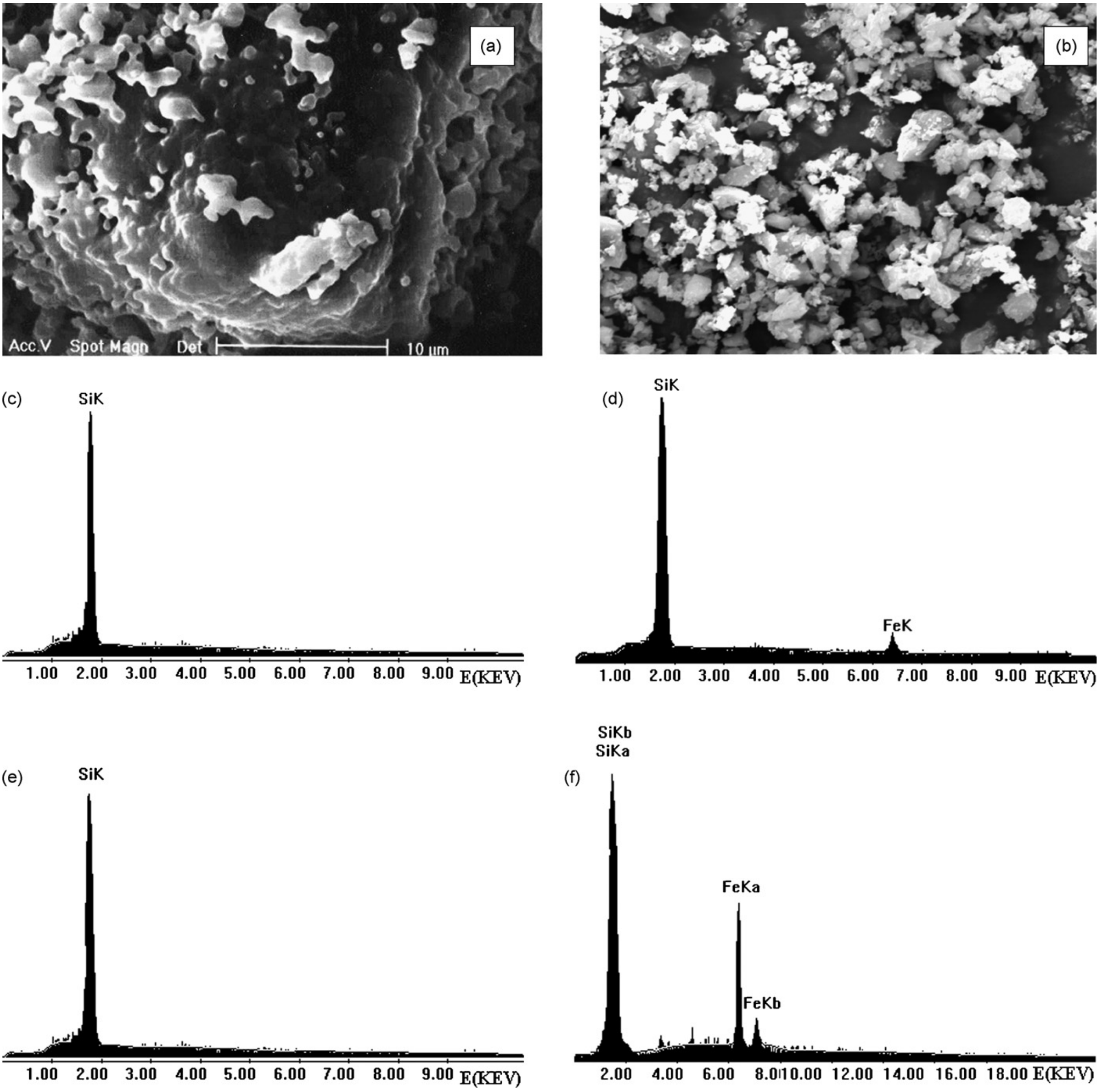

Fig. 4. Micrograph of $SiO_2$–$0.2Fe_2O_3$ powdered pigments heated at (a) 1300 °C and (b) 1200 °C for 4 h. The specific surface area of fumed silica was 200 $m^2$/g. (c) EDX of a no melting white particle of micrograph (a), (d) EDX of the local melting of micrograph (a), (e) EDX of white particle of micrograph (b) and (f) surface EDX of the matrix background of micrograph (b).

CIELAB method is usually accepted to specify the color of a product. This method measures the adsorption intensity in the visible region to obtain the three parameters $L^*$, $a^*$, and $b^*$, brightness, red/green and yellow/blue color intensities, respectively.

In Fig. 1, UV–vis spectra of heated powders show that red hue of pigments was more intense and brightness decreases with increasing hematite/silica mole ratio. As can be seen, these changes are not linear. The hematite/silica pigment with a mole ratio of 0.1 gives a red shade pigment but it is not enough to obtain a red shade in the mentioned glaze and it nearly tends to pink (Table 2). On the other hand, the red shade of the glaze which contains hematite/silica with a mole ratio of 0.4 is a little tending to maroon. Probably, suitable hematite/silica mole ratio depends on the chemical composition of the glaze. In fact, increasing the mole ratio of the hematite/silica decreases the protective action of silica. Gualtieri et al. [7] believe that aggressive boron-rich frits, which melt at low temperatures, favor silica decomposition into the glass phase and thus release hematite. Hematite in contact with an alkaline glass matrix becomes dark-brown, because the surface iron changes its chemical environment from six-fold to four-fold. Therefore, it may be that $SiO_2$–$0.4Fe_2O_3$ pigments in mentioned fritted glaze result in the introduction of some free hematite into the glass phase.

To optimize the synthesis conditions, the mole ratio of hematite/silica was fixed to 0.2. TGA measurement for the $SiO_2$–$0.2Fe_2O_3$ composition studied indicated two endothermic weight losses corresponding to the elimination of the humidity water and to the dehydroxylation of the iron(II) sulfate into iron oxide at temperatures of about 100 and 700 °C, respectively (Fig. 2).

All the heat treated samples (calcinations in the temperature range 1000–1300 °C for 4 h) were subjected to powder X-ray diffraction. Crystalline hematite was observed in all of the heat-treated samples (Fig. 3). No crystalline phases of silica were observed in any of the samples that were heated below 1100 °C. Above this temperature, sharp peaks of crystalline cristobalite were detected even if at 1300 °C the crystalline cristobalite peaks have lower intensity. This reduction is probably due to crystalline cristobalite transformation in amorphous phase. SEM observations (Fig. 4(a)) show some local melting of this powder while EDS of the melting location shows some partial diffusion of hematite into silica, confirming that the chemical environment of some surfaces containing $Fe_2O_3$ will be changed and dissolved in the melting silica.

Table 2
Effect of pigments composition on shade of fired glazes

| Pigments composition | $L^*/a^*/b^*$ of fired glazes |
|---|---|
| $SiO_2$–$0.1Fe_2O_3$ | 54.051/10.273/7.323 |
| $SiO_2$–$0.2Fe_2O_3$ | 44.122/21.76/14.38 |
| $SiO_2$–$0.3Fe_2O_3$ | 37.745/20.555/12.051 |
| $SiO_2$–$0.4Fe_2O_3$ | 35.37/16.22/12.91 |

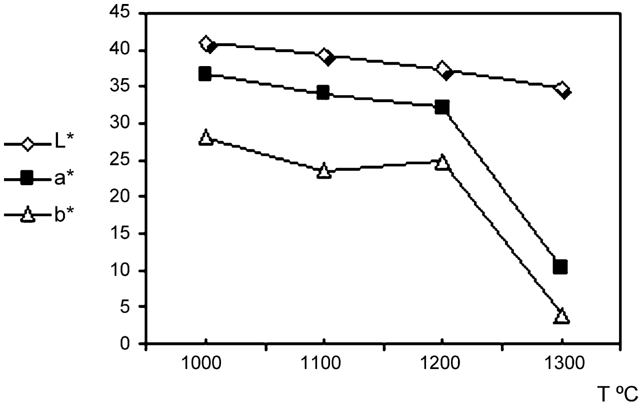

Fig. 5. Effect of calcination temperature on shade of $SiO_2$–$0.2Fe_2O_3$ powdered pigments heated for 4 h. The specific surface area of fumed silica was 255 $m^2/g$.

Table 3
Effect of synthesis temperature and specific surface area of fumed silica on shade of fired glazes ($SiO_2$–$0.2Fe_2O_3$ pigments)

| | $L^*/a^*/b^*$ of fired glazes | | |
|---|---|---|---|
| | 1000 °C | 1100 °C | 1200 °C |
| 200 $m^2/g$ | 39.004/17.964/14.668 | 45.33/19.734/12.37 | 43.968/21.35/13.89 |
| 255 $m^2/g$ | 38.366/15.264/14.832 | 48.328/21.472/15.0 | 44.122/21.76/14.38 |
| 390 $m^2/g$ | 34.029/20.796/23.97 | 52.025/22.16/13.78 | 50.565/23.136/15.14 |

Fig. 4(a) and (b) presents the microstructures of powdered pigments after calcinations and the effect of temperature on the sintering and crystallization of silica particles and consequently on the inclusion process. In all the investigated samples EDS of particles does not detect Fe peaks and just show Si peaks. It might be concluded that sintered cristobalite cover formed *in situ* on crystalline hematite particles.

Regarding the color behavior, $L^*$ values indicate that the degree of darkness of pigments slowly increases (Fig. 5) while $a^*$ factor evidently decreased, specially for samples which were heat treated at 1300 °C. Although $a^*$ value of pigment samples increases with increasing surface area of fumed silica, as shown in Fig. 6, their shades in glaze are not so different (Table 3).

No evident effects of the specific surface area of the fumed silica on the formation of the iron(III) oxide were observed. No crystalline compounds, derived from chemical solid state reactions between silica and hematite, were observed in any

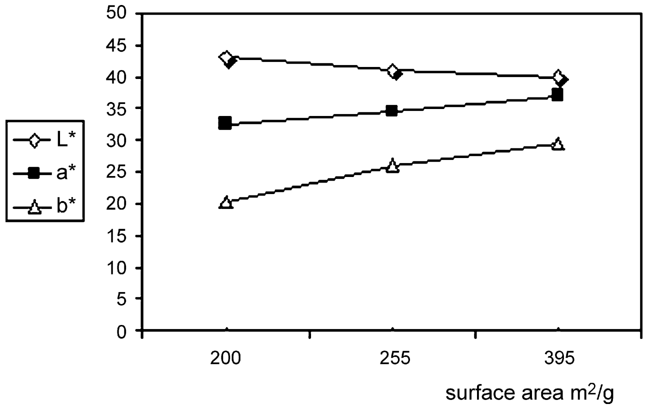

Fig. 6. Effect of specific surface area of fumed silica particles on shade of $SiO_2$–$0.2Fe_2O_3$ powdered pigments heated at 1100 °C for 4 h.

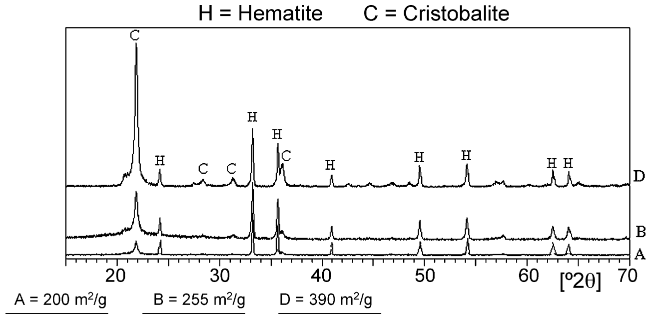

Fig. 7. XRD patterns of $SiO_2$–$0.2Fe_2O_3$ powdered heated pigments at 1100 °C for 4 h containing fumed silica with specific surface area of: (A) 200 $m^2/g$, (B) 255 $m^2/g$ and (D) 390 $m^2/g$.

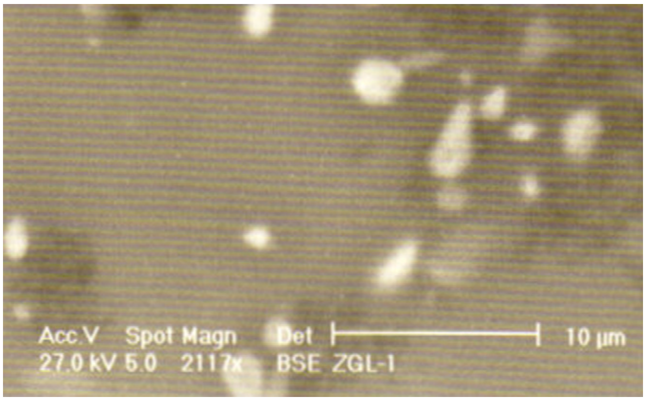

Fig. 8. SEM micrograph of the red glaze fired at 1000 °C containing 10 wt% of the $SiO_2$–$0.2Fe_2O_3$ powdered pigment heated at 1200 °C for 4 h; specific surface area of the fumed silica was 390 $m^2/g$.

sample obtained in the studied calcination temperature range [3,9]. The binary phase diagram of $SiO_2$–$Fe_2O_3$ indicates no reaction or compound between $SiO_2$ and $Fe_2O_3$ for all ratios [13]. The fumed silica with higher area has more surface energy and thus reactivity. It causes sharper peaks of cristobalite phase at 1100 °C (Fig. 7).

All of the pigments that were heat treated at 1000 °C independently from the surface area, are not stable in the glazes that result brown shade (Table 3). Higher stability is shown by the pigments heat treated at 1100 and 1200 °C due to the effective cristobalite covering of hematite. In Fig. 8, SEM observation of the red glaze fired at 1000 °C displayed the pigment particles that were stable in the glossy glaze. EDS of these particles shows only Si peaks which confirms stability of cristobalite crystals. This is also confirmed by XRD pattern of the powdered red glaze which shows very intensive peaks of cristobalite (Fig. 9).

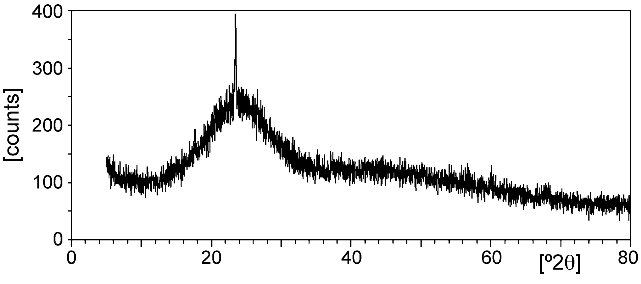

Fig. 9. XRD pattern of the red glaze fired at 1000 °C containing 10 wt% of the $SiO_2$–$0.2Fe_2O_3$ powdered pigment heated at 1200 °C for 4 h; specific surface area of the fumed silica was 390 $m^2/g$.

## 4. Conclusions

In order to prepare a hematite–silica inclusion red ceramic pigment by a conventional ceramic process, fumed silica with different surface areas and iron(II) sulfate were used. Submicron silica particles sintered and crystallized to cristobalite occluding and covering the small crystalline particles of *in situ* formed hematite starting from 1100 °C.

The better conditions for sintering of amorphous nano-size particles of fumed silica with iron(II) sulfate were found to be 1100–1200 °C for 4 h. Calcination temperatures must not be over 1200 °C to prevent the darkness of red shade of pigment. It was shown that specific surface area of the fumed silica has no effect on thermal and chemical stability of the pigment, but higher surface area promotes silica crystallization.

Due to its chemical and thermal stability, this heteromorphic pigment may be considered to be a suitable red pigment for ceramic applications.

## Acknowledgements

We are grateful to Professor Tiziano Manfredini, and Federica Bondioli from Material Engineering Department of Modena and Reggio Emilia University (DIMA) and Professor H. Assadi for reviewing the manuscript and to Mr. Rezaie for his help with the SEM studies. Thanks are also expressed to the Iran Color Research Center for the provision of the experimental facilities for color measurements and to Mashad Glaze Company for the provision of the glaze used.

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