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Effect of the surfactant and precipitant on the synthesis of pink coral by a microemulsion method

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Abstract

The use of hematite and other iron oxides as a natural red ceramic pigment has been known since prehistoric times and, probably, is the first ceramic pigment to have been employed by humanity. However, hematite crystals grow with temperature and the colour shade becomes unstable. The best red shades are obtained by the inclusion of hematite in silica or in zircon (pink coral) casings. A microemulsion method has been applied in order to improve the inclusion efficiency of hematite into zircon crystals; the effects of several parameters on the synthesis, such as the precipitating agent (ammonia or alkaline hydroxides), the surfactant (anionic or cationic) and the flux agent (NaF or NaF.2NaCl), have been studied.

Keywords: Coral; Emulsions; Fe_2O_3; Pigments; $ZrSiO_4$

1. Introduction

The use of hematite and other iron oxides as natural red ceramic pigments has been practised since prehistoric times. The only red pigments known up to 1683 were the iron oxides and the red of copper, which requires CO atmosphere because the chromophore agent (Cu^+) is unstable in oxidising media. In 1683 Cassius Von Leyden prepared the Au–Sn purple ceramic pigment.[1]

The iron(III) oxides suffer a reduction to Fe^{2+} ion, promoted by the emission of molecular oxygen according to Eq. (1), when fired at high temperature or when in the presence of unoxidised organic material.

$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + 1/2\ O_2 \quad (1)$$

Together with this reduction process, the hematite crystals grow with temperature and the colour shade becomes unstable. To stabilise the red colour it is necessary to incorporate the Fe^{3+} ion into a stable lattice or to encapsulate the hematite crystals into a stable crystal host.[2] When Fe^{3+} is stabilised by the introduction into a spinel structure such as $NiFe_2O_4$ the colour becomes brown. The best red shades are obtained by inclusion of hematite in silica or in zircon (pink coral).[3–5]

In order to achieve an effective encapsulation of the cromophore agent into the crystal host, the sintering and/or crystallisation of the matrix must be synchronised with nucleation-growth of the included chromophore phase. The crystallisation, sintering and inclusion processes are thus required to take place simultaneously. Consequently, control of particle size of the raw powder will go towards high levels in encapsulation. Traditional ceramic processing is limited by the diffusional barrier that prevents the control of the microstructural heterogeneity,[6] and the nucleation and growth processes, and thereby the reactivity of the system.

In order to avoid this problem, a microemulsion route has been applied so as to improve the microstructural characteristics. A microemulsion is a microheterogeneous system which provides a large interfacial area and low viscosity. Usually, microemulsion systems contain water, oil, a surfactant, and often a cosurfactant in order to stabilise the system.[7] The microemulsion of the precursors is formed by forming droplets of water containing the soluble precursors of the product, suspended and stabilised in an organic non-polar solvent (usually iso-octane). The stabilisation of the micro-

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emulsion is reached by addition of an appropriate surfactant and using ultrasonic activation. The emulsion droplets of precursors were treated with a microemulsion of alkali suspended in the same organic non-polar solvent. Microspherical droplets activated by ultrasonic agitation then coalescence, yielding the final microemulsioned precipitation product (Fig. 1).

The microemulsion method has been applied and the effects of several parameters on the synthesis, such as the nature of precipitating agent (ammonia or alkaline hydroxides), the surfactant (anionic or cationic nature) and the flux agent (NaF or NaF.2NaCl) have been studied. The addition of halide salts as mineralisers for the system has been analysed because it is a usually practice in the commercial synthesis of pink coral pigment. The results are compared with a sample with the same composition of the microemulsioned samples but using oxides (ZrO_2 and quartz) as raw materials following a classical ceramic method.

2. Experimental

Iron zircon samples of molar composition $0.4Fe_2O_3:ZrSiO_4:0.2M$ (where M are the flux agent NaF or NaF.2NaCl), have been prepared by microemulsion (ME) synthesis route and by a ceramic method (CE) The precursors used in the samples are shown in Table 1.

The ceramic sample (CE), were prepared by ball milling the precursors in acetone media. In the other hand, the microemulsion samples were prepared according to the procedure shown in Fig. 2. The microemulsion of the precursors was obtained by mixing the 0.5 M aqueous solution with iso-octane (oil phase), the surfactant agent (3 wt.% of *N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide, alkylbenzildimethylammonium chloride or sodium laurylsulphonate have been used), and co-surfactant (1 wt.% of 1-propanol). The mixture was stirred for 30 min and then was kept in ultrasonic agitation for 30 min. A similar procedure was followed to prepare the ammonia microemulsion. The microemulsion of precursors and the precipitant microemulsion were mixed by ultrasonic agitation for 1 h. In the resulting microemulsion, three different phases could be distinguished: an upper organic (iso-octane) phase, an aqueous phase at the bottom, and the intermediate product layer. The iso-octane phase was removed, and the microemulsioned raw powder was obtained by drying the remainder at 110 °C in an oven.

Samples were fired at 1000 °C in an electrical furnace, with a soaking time of 2.5 h. The fired samples were micronised and washed in a ball-mill in water media and dried at 110 °C. The micronised powders were tested as ceramic pigments for glazes using a conventional monoporosa glaze. The composition of this glaze is indicated in Eq. (2).

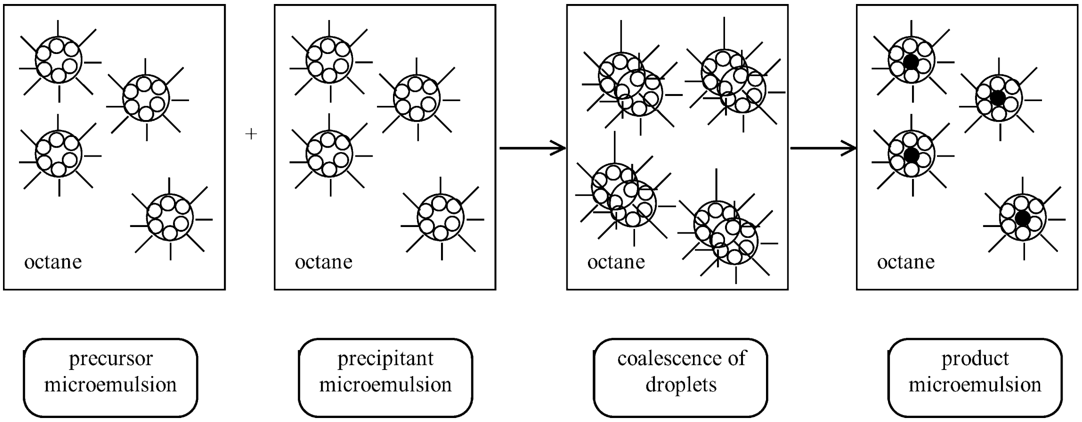

Fig. 1. Microemulsion mechanism[8].

Table 1
Precursors of samples

Sample	Method (precipitant and surfactant)	Precursors (from Aldrich S.A.)
CEI	Ceramic	ZrO_2, Quartz, $FeSO_4.7H_2O$, NaF.
ME1	Microemulsion with *N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide and NH_3	LUDOX(32% in SiO_2), zirconium acetate (21% in ZrO_2), $FeSO_4.7H_2O$
ME2	Microemulsion with *N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide and NaOH	LUDOX(32% in SiO_2), zirconium acetate (21% in ZrO_2), $FeSO_4.7H_2O$
ME3	Microemulsion with alkylbencildimethylammonium and NH_3	LUDOX(32% in SiO_2), zirconium acetate (21% in ZrO_2), $FeSO_4.7H_2O$
ME4	Microemulsion with alkylbencildimethylammonium and NaOH	LUDOX(32% in SiO_2), zirconium acetate (21% in ZrO_2), $FeSO_4.7H_2O$
ME5	Microemulsion with sodium laurylsulphonate and NH_3	LUDOX(32% in SiO_2), zirconium acetate (21% in ZrO_2), $FeSO_4.7H_2O$
ME6	Microemulsion with sodium laurylsulphonate and NaOH	LUDOX(32% in SiO_2), zirconium acetate (21% in ZrO_2), $FeSO_4.7H_2O$

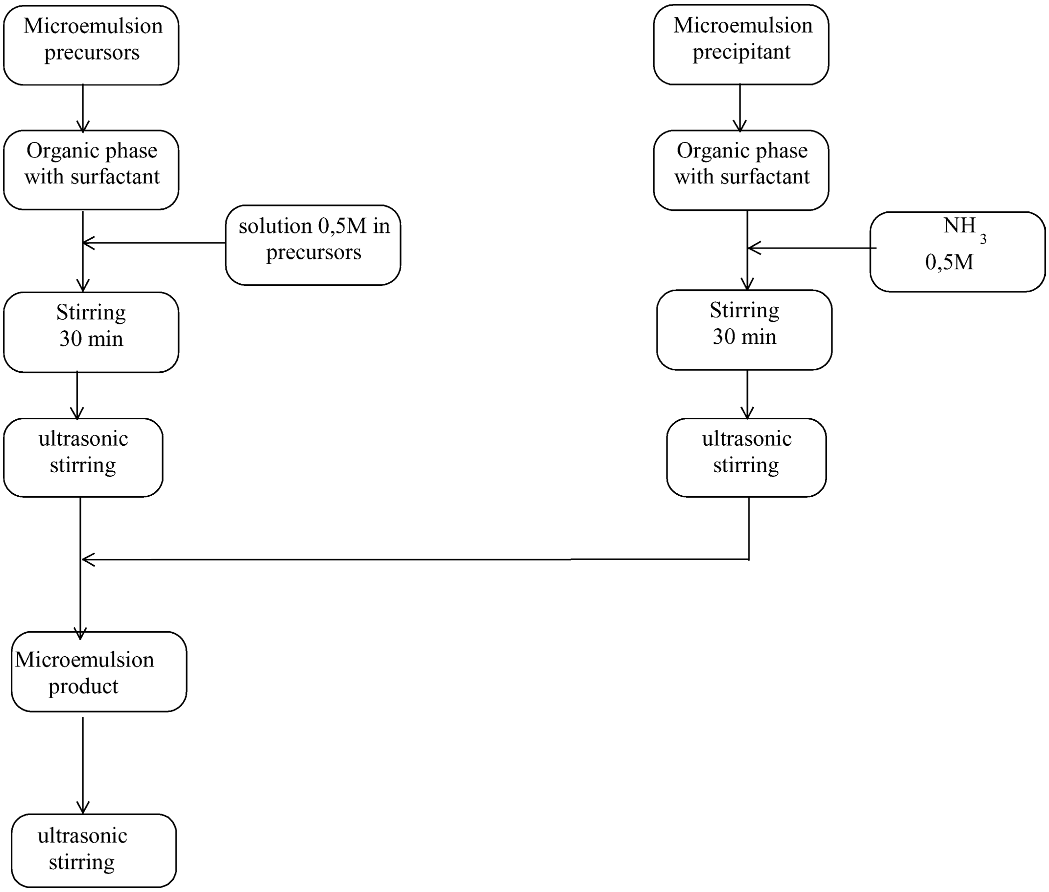

Fig. 2. Microemulsion method.

$$\begin{array}{llllll} K_2O & 0.126 & & & & \\ CaO & 0.565 & Al_2O_3 & 0.323 & SiO_2 & 1.972 \\ ZnO & 0.329 & & & & \end{array} \qquad (2)$$

In the enamelling process, 5 g of ceramic pigment and 60 g of water were mixed with 95 g of glaze, then the mixture were ball milled. The resulting slip was deposited on a ceramic biscuit by the conventional doctor blade procedure. The raw tile was fired in a fast-firing Nanetti furnace at 1085 °C, with a 50 min cold-to-cold firing cycle.

X-Ray diffraction patterns were obtained using conventional powder techniques in a Siemens diffractometer (D500 model) with CuK_α radiation Ni-filtered.

Microstructure characterisation of powders was carried out by scanning electron microscopy (SEM), using a Leo-440i Leech microscope.

UV-V-NIR (ultraviolet visible near infrared) spectroscopy of enamelled samples mentioned above was carried out in a Lambda 2000 Perkin-Elmer spectrophotometer by diffuse reflectance technique.

The colourimetric $L^*a^*b^*$ parameters of the enamelled samples were measured following the CIE (Commision Internationale de L'Eclariage) colourimetric method[9] using a Perkin-Elmer spectrophotometer, with standard lighting C. On this method, L^* is the lightness axis black (0)→ white (100), a^* is the green (−)→ red (+) axis, and b^* is the blue (−)→ yellow (+) axis.

The magnetic characteristics of the samples has been measured in an AGFM (magnetometer of variable gradient field) magnetosusceptometer which measures the magnetisation interval between 1 μemu and 5 emu with 10 nemu of sensitivity, using an applied field varying from −10.000 to 10.000 Oe.

3. Results and discussion

3.1. XRD and DTA-TG calorimetric analysis of samples

The XRD results are shown in Table 2. In the case of the raw powders, the ceramic sample presents the peaks associated with the crystalline precursors; and all microemulsioned samples are amorphous in XRD, the ME2 sample (sodium hydroxide and *N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide microemulsioned sample) being the only one to show weak peaks associated with thenardite (Fig. 3).

Table 2
XRD evolution of crystalline phases in samples and CIE $L^*a^*b^*$ of fired powders 5% enamelled in a conventional glaze

Sample	Raw powder	ATD-TG (unfluxed residue)	Unfluxed 1000 °C	NaF 1000 °C	NaF.2NaCl 1000 °C
CE	B,Q,F(s)	B,Q(s)H(w)	Z,Q(s)B,H(w) 63/4/12	Z(s)H(vw) 65/15/7	Z(m)B,H(w) 71/11/8
ME1	A	E(m)H(w)	Z,B(m)Q,H(w) 73/10/19	Z(m)B,H(w) 64/12/7	Z,B(m)H(w) 76/10/14
ME2	T(w)	A	B,G,P(m)Q(w) 82/5/18	B(m)G,H(w) colourless	B(m)G,H(w) colourless
ME3	A	P,B,M,E(w)	B(m)Q,T(w) 70/8/12	Z(m)B,H(w) 64/11/4	Z(s)B,H(w) 69/14/13
ME4	A	E(m)H(w)	B(m)Q,H(w) 69/10/14	Z(m)B,H(w) 65/13/6	Z(s)B,H(w) 70/15/12
ME5	A	E(m)H(w)	Z(m)B,Q,E(w) 66/15/18	sintering	Z(s)B,H,Q(w) 75/15/21
ME6	A	sintering	sintering	sintering	sintering

Crystalline phases: Z(zircon), B(baddeleyite or monoclinic ZrO_2), E(tetragonal ZrO_2), Q(quartz), H(hematite Fe_2O_3), F($FeSO_4.7H_2O$),M(maghemite Fe_3O_4), Fe_3O_4), S($(NH_4)_2SO_4$), N(Na_2SO_4),T(thenardite Na_2SO_4), G($Na_4ZrSi_3O_{11}$),P(Na_2ZrSiO_5).

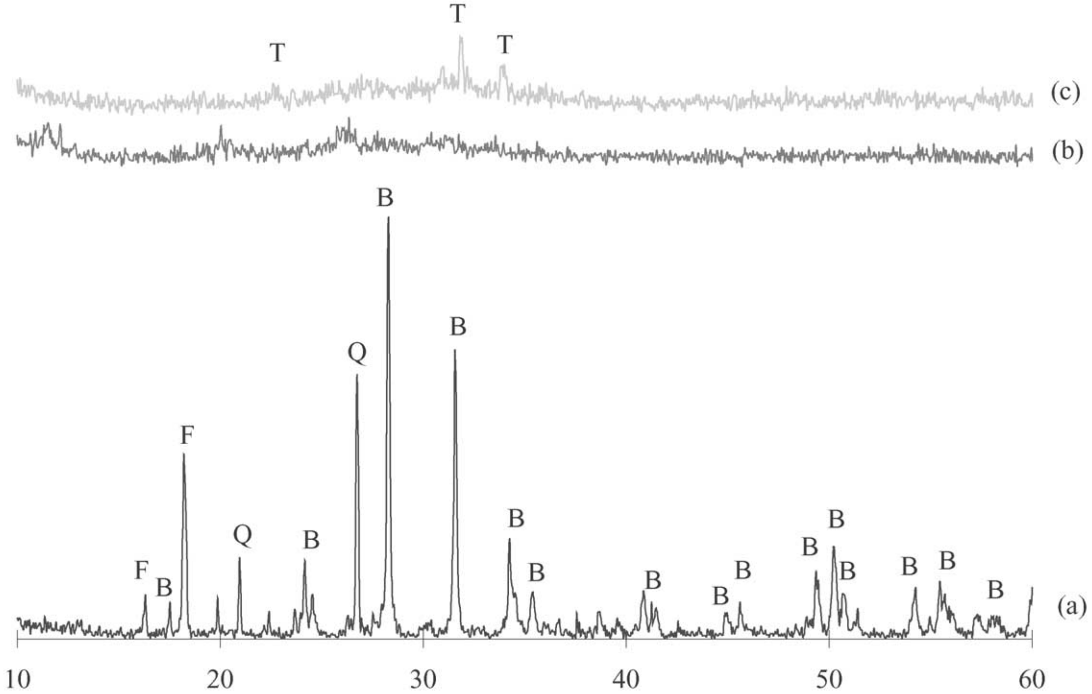

Fig. 3. XRD of microemulsion raw dried powders: (a) CE, (b) ME3, (c) ME2: B(baddeleyite or monoclinic ZrO_2), Q(quartz), T(thenardite Na_2SO_4).

The DTA-TG analysis of several samples is shown in Fig. 4. The CE sample (Fig. 4a) shows three bands: the endothermic band at 110 °C is associated with the loss of the first six molecules of water from $FeSO_4.7H_2O$, the endothermic band at 480 °C is due to the elimination of the seventh molecule of water and iron sulphate decomposition occurs at 620 °C (endothermic)[10]. XRD of the residual DTA/TG samples (Table 1), shows strong peaks of monoclinic zirconia and weak peaks of quartz and hematite in the case of CE sample. In all DTA/TG of the microemulsioned samples (Fig. 4b), three characteristic bands appear at 90 °C (endothermic), 350 °C (exothermic) and 700 °C (endothermic), due to loss of water hydration, organics combustion, and sulphate decomposition respectively. XRD of residual DTA/TG samples gives evidence for the presence of tetragonal zirconia and hematite as a secondary phase, but using the NaOH precipitant the sample (ME2) remains amorphous and the sample ME6 sintered and was discarded (Table 2).

3.2. *Unfluxed samples*

From the XRD results of the fired unfluxed samples (Table 2), it can be observed that only when using the ammonia precipitant in ME1 (ammonia-*N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide) and ME5 (ammonia-laurylsulphate) does the system react to form zircon. The M6 (NaOH-laurylsulphate) sintered, and therefore, is discarded as a ceramic pigment. The rest of the samples do not react to form zircon. The ME2 microemulsioned sample using NaOH (Fig. 5), stabilises the $Na_4ZrSi_3O_{11}$ and Na_2ZrSiO_5 silicozirconates and are unable to produce red colour when glazed (see CIE $L^*a^*b^*$ values in Table 2); the brown colour obtained can be associated to hematite-silica system.[3,4] The ME3

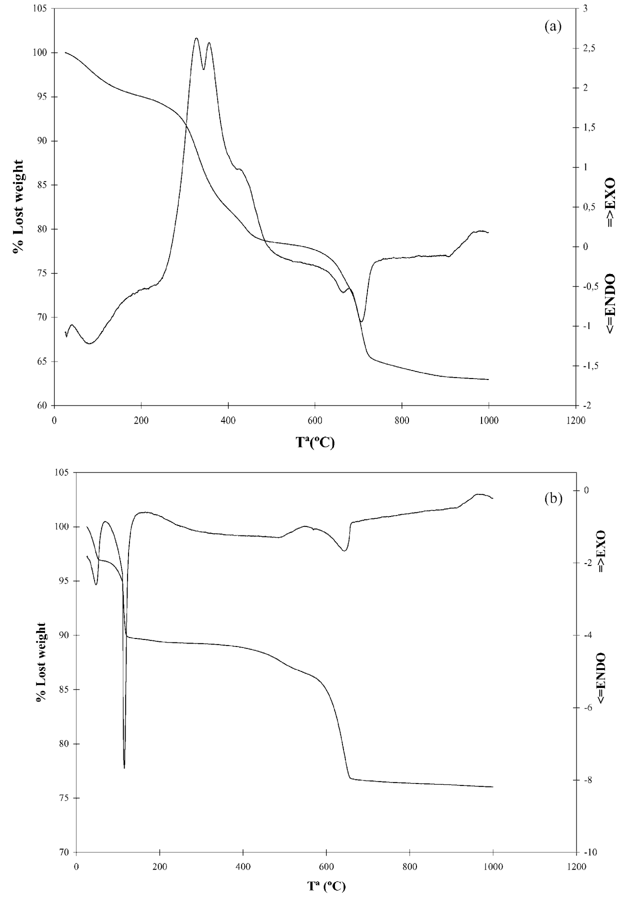

Fig. 4. DTA-TG analysis of indicated samples. (a) CE and (b) ME2.

sample (ammonia-alkylbenzildimethylammonium chloride) shows the presence of undecomposed thenardite by XRD and the brown colour obtained by glazing is due also to the hematite-quartz system, this sample shows maghemite instead hematite after ATD-TG treatment, indicating a specific effect of the alkylbenzildimethylammonium on the reactivity of the system. Only the reacted ME1 and ME5 samples give reddish colour when enamelled.

3.3. Results for the mineralised samples

The XRD results obtained for the NaF fluxed samples are shown in Fig. 6. The presence of the NaF improves the reactivity of the system: the CE sample show the best reactivity; samples ME5 and ME6 (surfacted by sodium laurylsulphate) sintered and were discarded; only ME2 remains unreacted and the rest of the microemulsioned samples show zircon peaks of medium intensity. All reacted samples show red colours when glazed, the ceramic CE sample shows the best red shade ($L^*a^*b^* = 65/15/7$).

The XRD results using NaF.2NaCl flux agent are shown in Fig. 7. The CE sample had less zircon reactivity and red colour shade compared with the NaF fluxed sample; the ME2 sample does not react; ME6 sintered and the rest of the samples had greater reactivity when referred to the NaF fluxed samples, producing reddish-yellow colours (high b^*) slightly less intense (low L^*).

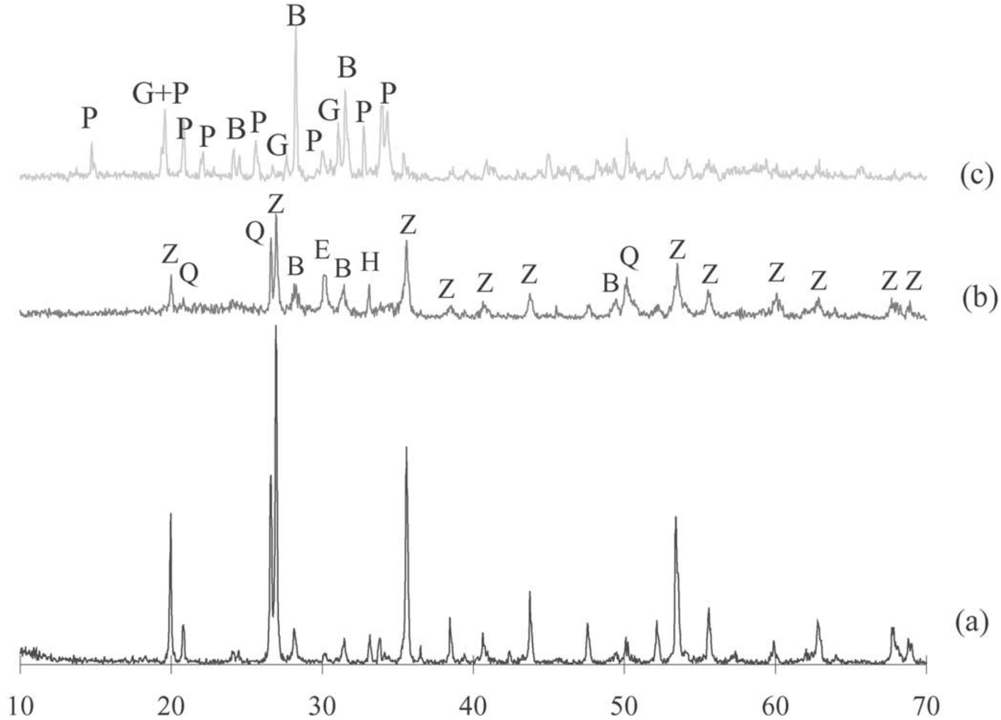

Fig. 5. XDR of unfluxed samples fired at 1000 °C/2.5 h: (a) CE, (b) ME5, (c) ME2. Z(zircon), B(baddeleyite or monoclinic ZrO_2), E(tetragonal ZrO_2), Q(quartz), H(hematite Fe_2O_3), G($Na_4ZrSi_3O_{11}$),P(Na_2ZrSiO_5).

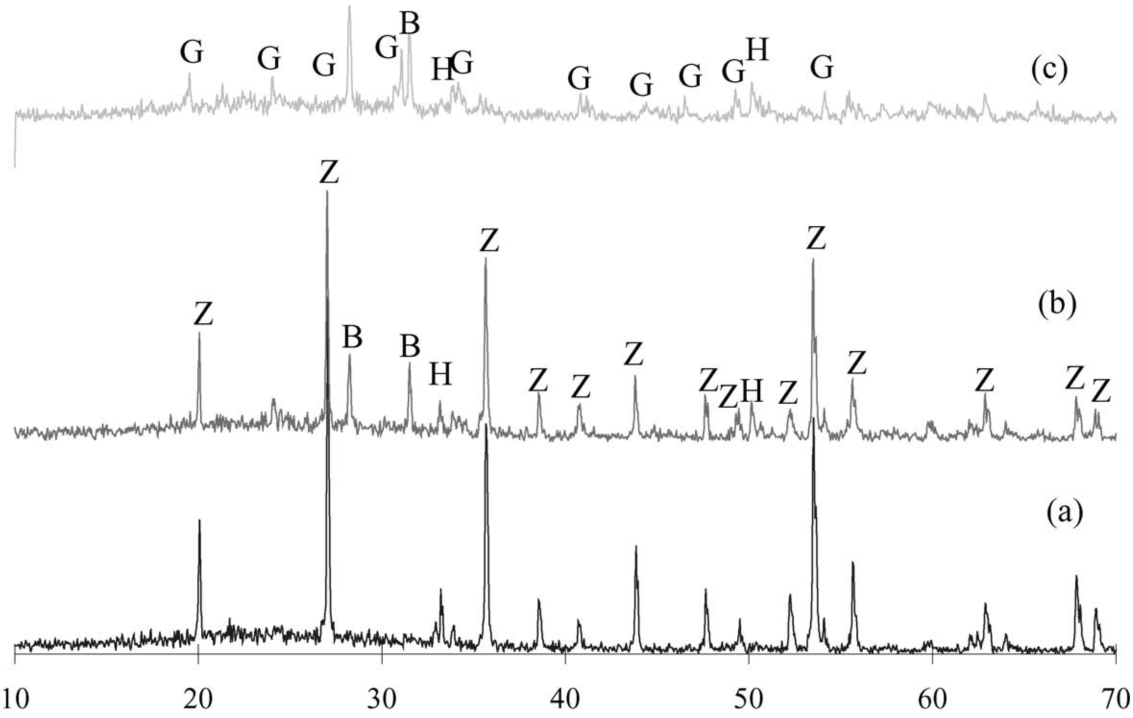

Fig. 6. XRD of NaF fluxed samples fired at 1000 °C/2.5 h: (a) CE, (b) ME4, (c) ME2. Z(zircon), B(baddeleyite or monoclinic ZrO_2), H(hematite Fe_2O_3), F($FeSO_4.7H_2O$), G($Na_4ZrSi_3O_{11}$).

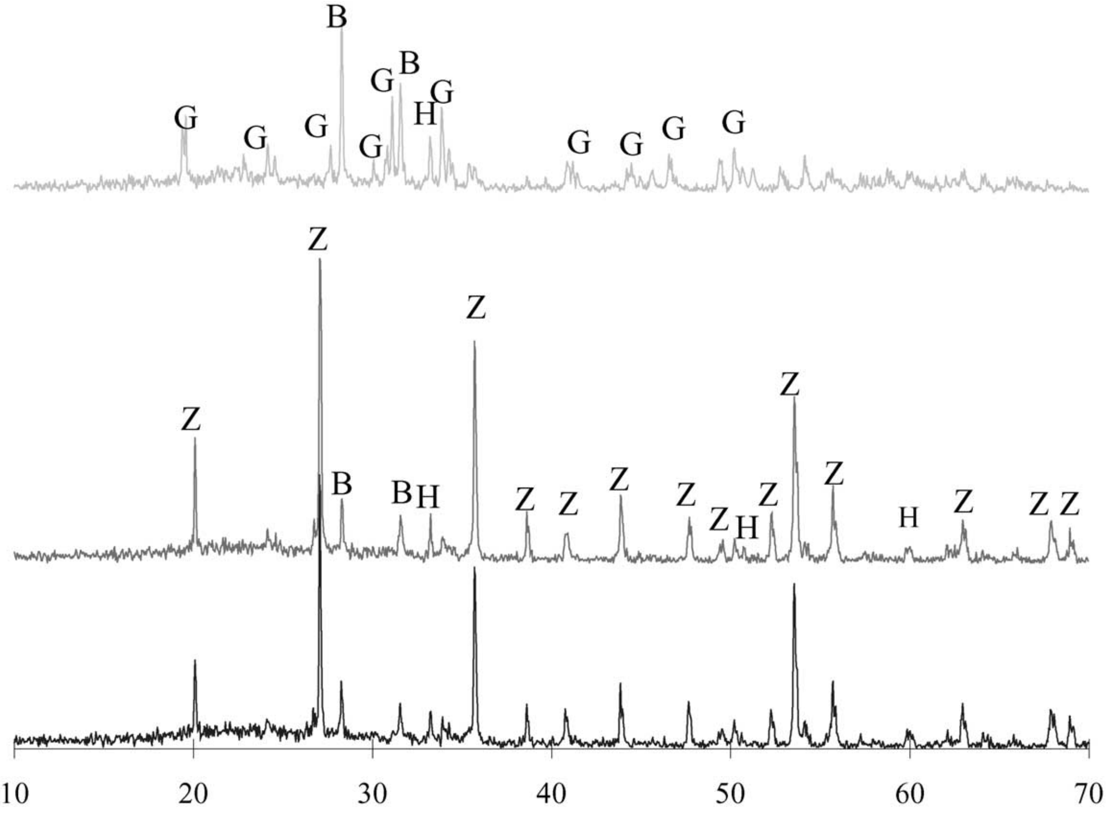

Fig. 7. XRD of NaF.2NaCl fluxed samples fired at 1000 °C/2.5 h: (a) CE, (b) ME3, (c) ME2. Z(zircon), B(baddeleyite or monoclinic ZrO_2), H(hematite Fe_2O_3), G($Na_4ZrSi_3O_{11}$).

3.4. *Effect of the surfactant agent*

It can be stated as an important effect of the surfactant agent that alkylbenzildimethylammonium chloride presents the best results in the fluxed samples independently of the precipitant agent; however, it does not react in absence of the flux agent. On the other hand, the *N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide and sodium laurylsulphonate react and give a red colour without the need for fluxing. Likewise the role of the precipitant agent is important: NaOH microemulsioned samples do not react using *N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide and sinter using laurylsulphonate as surfactant agent respectively. Ammonia shows the best result for both zircon reactivity and red colour shade. Finally, the flux agent shows different behaviour: NaF produces more

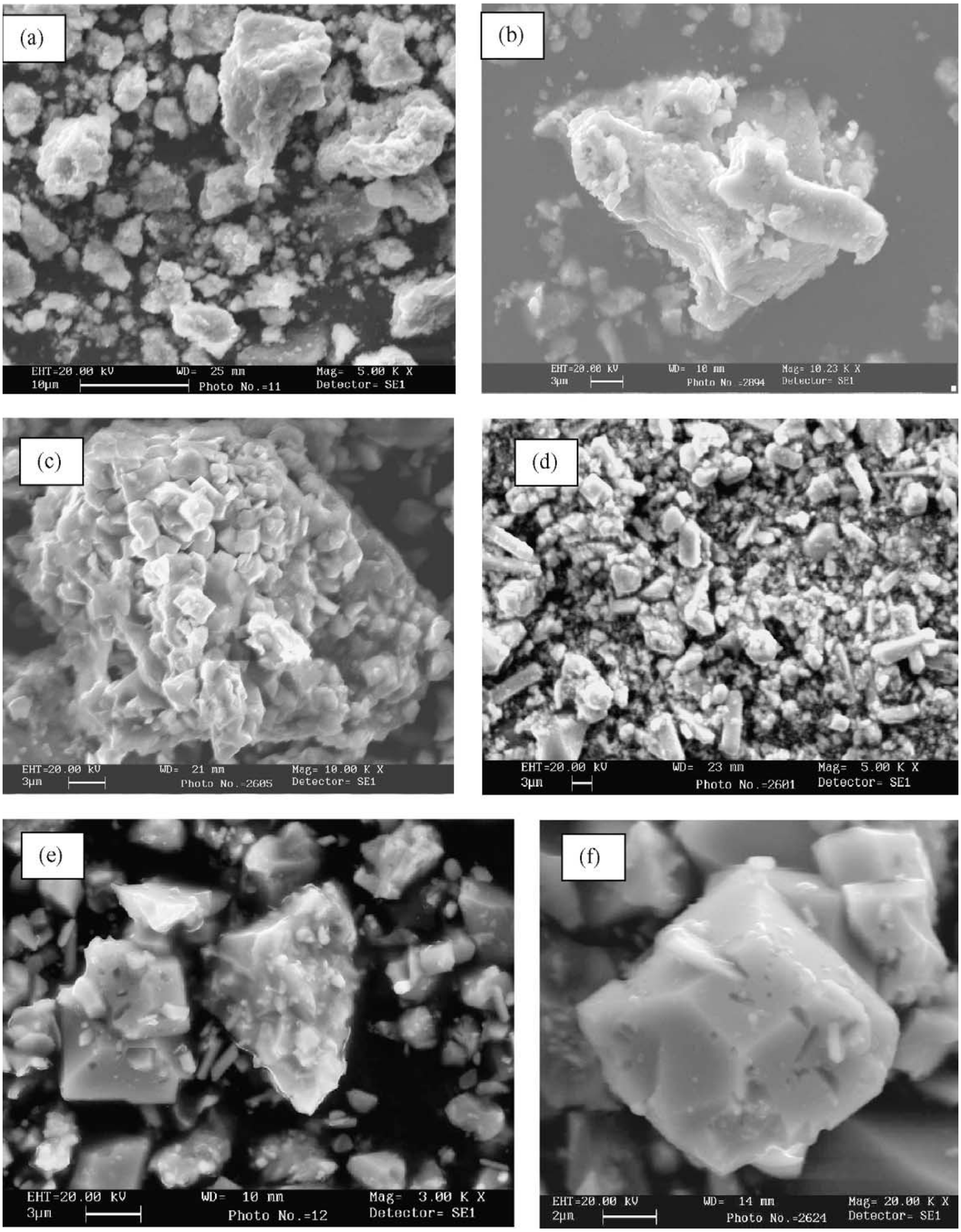

Fig. 8. Micrographs of samples fired at 1000 °C/2.5 h : (a) ME1 unfluxed, (b) ME4 unfluxed, (c) CE NaF fluxed, (d) ME2 NaF fluxed, (e) ME4 NaF.2NaCl fluxed, (f) ME5 NaF.2NaCl fluxed.

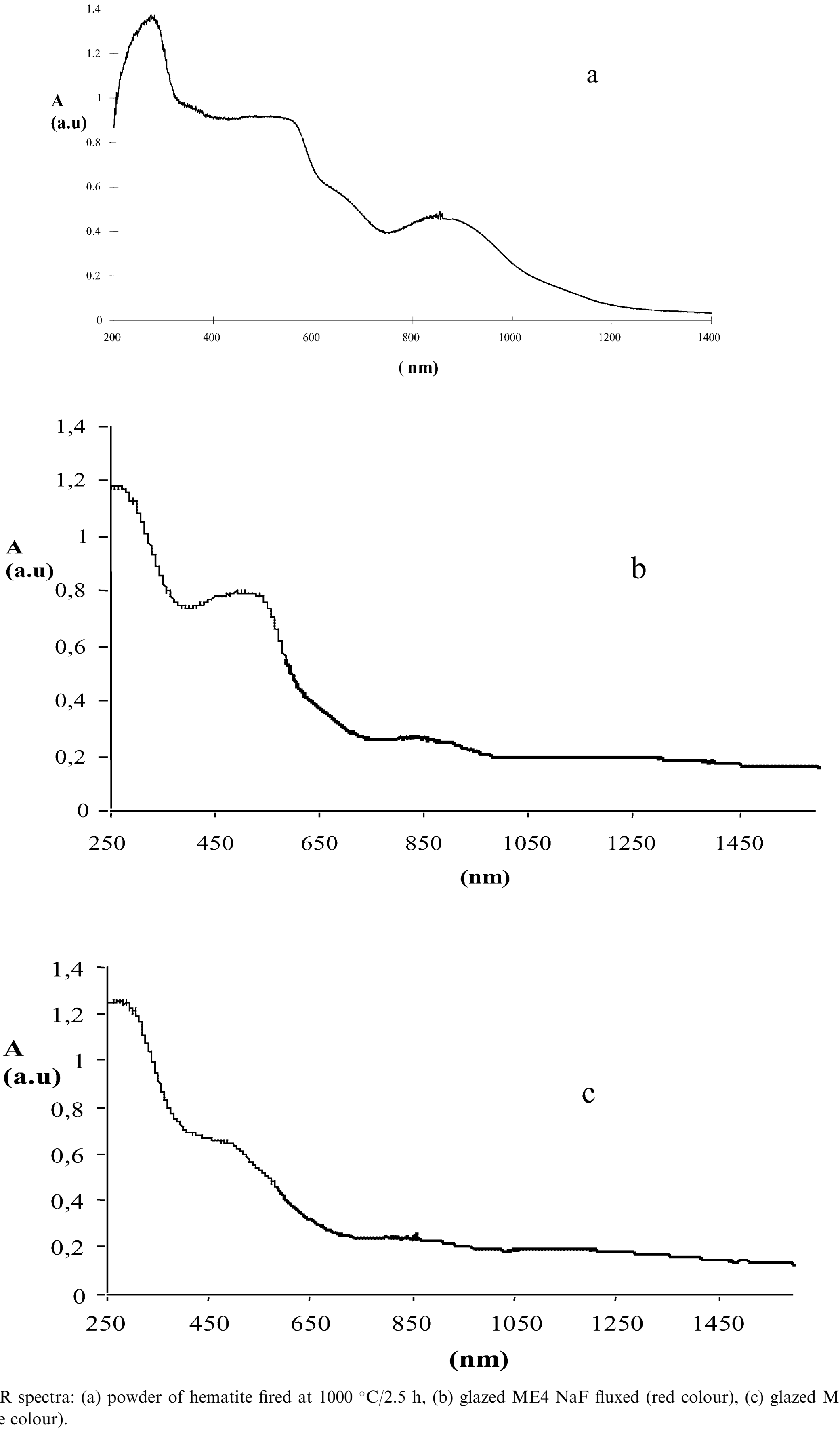

Fig. 9. UV-V-NIR spectra: (a) powder of hematite fired at 1000 °C/2.5 h, (b) glazed ME4 NaF fluxed (red colour), (c) glazed ME4 NaF.2NaCl fluxed (red-orange colour).

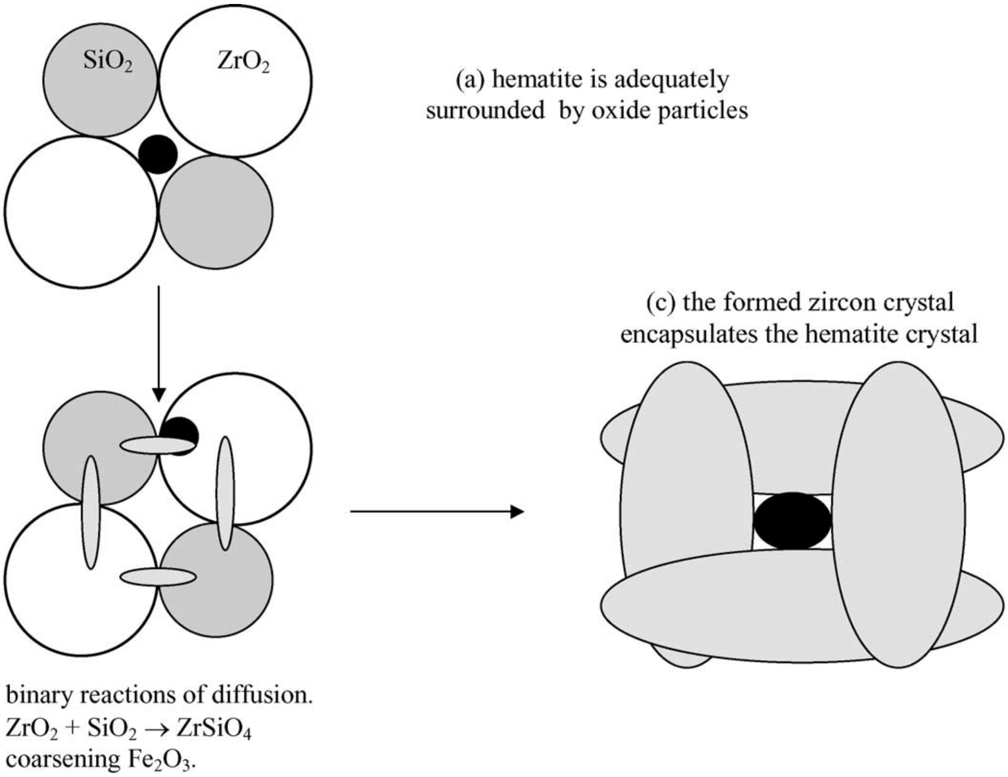

Fig. 10. Ideal model for pink coral ceramic pigment.

intense (low L^*) and less yellow (low b^*) but also less red (a^*) than NaF.2NaCl agent, NaF gives red shades and NaF.2NaCl red-orange colour shades.

3.5. Microstructure of the samples

The microstructure of the samples observed by SEM is shown in Fig. 8. It can be observed that there are coarse aggregates in zircon reacted unfluxed samples such as ME1 and ME5, which are able to produce colour (Fig. 7a), in contrast, the unreacted unfluxed samples show micrometric particles which do not produce colour when glazed (Fig. 7b). The NaF fluxed samples show aggregates of regular crystals of zircon, 1 µm sized independently of the method (Fig. 7c), but if the sample does not react, irregular particles can be observed (Fig. 7d). Finally, NaF.2NaCl zircon reacted powders show large single regular crystals of zircon around 2–4 µm in size (Fig. 7e–f).

3.6. UV-V-NIR spectroscopy

The UV-V-NIR spectra for raw hematite fired at 1000 °C and representative glazed samples are shown in Fig. 9. The colour in the glazed samples is associated with the presence of hematite protected into zircon crystals and the intensity of the reddish colour is proportional to the degree of protected hematite. In effect, fired raw hematite shows a band centred at 850 nm and two shoulders at 700 and 580 nm respectively; finally, an intense band at 290 nm is detected in the UV-V-NIR spectrum (Fig. 8a). The hematite spectrum is displayed with high intensity in the red coloured samples ($L^*a^*b^* \approx 65/15/7$) and diminishes in the red-orange coloured samples ($L^*a^*b^* \approx 70/15/13$).

3.7. Magnetisation measurements

The measurements of magnetisation (saturation M_s) carried out between LNT (liquid nitrogen temperature) and room temperature on these samples (CE, CO2, ME2) fall around 350 memu/g for orange-brown powders (ME1 and ME5 unfluxed) and diminish to 225 memu/g for red coloured samples (zircon reacted NaF or NaF.2NaCl fluxed samples). Finally for the brown sample (CE unfluxed sample), M_s reaches 3000 memu/g probably associated with a reduced form of hematite (amorphous Fe_3O_4). This reduction behaviour can be avoided by including hematite into the zircon crystals.

3.8. Structure of the pink coral ideal pigment

The ideal inclusion of hematite crystals into zircon host needs the synchronisation between the crystallization-sintering of the zircon and the nucleation-growth of the hematite.[5] The ideal model for pink coral formation is described in Fig. 10: (a) the hematite must be adequately surrounded in the raw mixture, (b) firing in the presence of the flux agent, the hematite growth, and zircon crystallise by diffusion mechanisms, and (c) the zircon crystal encapsulates the hematite crystal, which acts as chromophore agent. In this model, the high homogenisation of raw mixture can favours the process, however, if hematite growths too much (and reduces to magnetite), it is not efficiently encapsulated, likewise, if zircon did not crystallise in a sufficiently size the encapsulation did not progress neither.

The results discussed above are in agreement with the encapsulation model. In effect, the UV-V-NIR spectroscopy indicates that the spectrum of enamelled samples show a similar feature to the hematite powder spectrum; consequently, hematite can be associated with the chromophore agent in the system. However, if zircon does not crystallise, the pigment is not obtained (ME2 sample); if zircon shows an adequate size, the encapsulation are effectiveness and red colours are obtained (NaF mineralised samples), but if the sintering of zircon progress too much, the sintered material must be discarded as ceramic pigment. The microemulsion method produces homogeneous mixtures usually amorphous in XRD and their zircon reactivity and colouring properties depends strongly of the conditions of the microemulsion.

4. Conclusions

1. The ircon reactivy and colour of samples depends strongly on the conditions of the microemulsion such as surfactant, precipitant or flux agent.
2. Alkyltrimethylammonium chloride produces the best zircon reactivity and reddish colour using flux agent addition, but does not react without a mineraliser.
3. Ammonia produces amorphous microemulsioned powders that show high zircon reactivity and high hematite inclusion effectiveness giving red colours when glazed.
4. NaOH 6M used as precipitating agent shows a very different behaviour: it reacts and stabilises $Na_4ZrSi_3O_{11}$ and Na_2ZrSiO_5 silicozirconates avoiding the zircon crystallization using *N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide, but show amorphous microemulsioned powders that react and produce red colours when using alkyltrimethylammonium chloride; it gives sintered material when using laurylsulphonate as flux agent.
5. NaF acts better than NaF.2NaCl in order to encapsulate hematite, giving reddish colours. This fact is associated to the greater growth of zircon crystals when using NaF.2NaCl flux agent.
6. The results obtained by microemulsion procedure are in agreement with the encapsulation model of hematite into zircon usually accepted for the pink coral ceramic pigment.

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