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# Chemical state and distribution of Mn ions in Mn-doped $\alpha$-$Al_2O_3$ solid solutions prepared in the absence and the presence of fluxes

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**Abstract**

We have investigated the oxidation state and localization of the Mn cations in the corundum lattice for Mn-doped $\alpha$-alumina pigments prepared in the absence and the presence of fluxes by mainly using XPS, XANES and EXAFS techniques. It was found that irrespective of the preparation method, the pink colour of the pigments is mainly due to Mn(III) species dissolved in the corundum lattice, in which they form cluster containing $\sim$2 Mn cations. The more intense colour presented by the sample prepared in the presence of fluxes is due to the incorporation of a higher amount of Mn to the alumina lattice as a consequence of the presence of liquid phase which favours the diffusion process involved in the solid solution formation.


*Keywords:* $Al_2O_3$; Colour; Fluxes; Spectroscopy; Transition metal oxides; X-ray methods

## 1. Introduction

One of the most important technological applications of manganese-doped corundum ($\alpha$-$Al_2O_3$) powders is found in the ceramic industry in which, they have been used for long time as pink pigments.[1] In spite of this, little information can be found in literature regarding with the structural characterization of this system and the oxidation state of the Mn ions. Thus, although it has been assumed that this pigment consists of a Mn-corundum solid solution in which, the Mn cations are trivalent,[2] the experimental confirmation of such an assumption has not been reported. In fact, the only few works that deal with the chemical state of Mn in this system have suggested, on the basis of ESR measurements carried out for Mn-doped corundum single crystals, that the Mn cations can be incorporated into this oxide matrix in several oxidation states such as Mn(II),[3] Mn(III)[4] and Mn(IV).[5] Therefore, it seems desirable a more detailed investigation on the Mn valence in the Mn-alumina pigments, which is the main aim of this paper. For this purpose, we have mainly used X-ray photoelectron (XPS) and X-ray adsorption (XANES and EXAFS) spectroscopies. The later technique has been also used to gain information on the atomic environment of the Mn cations, which along with their chemical state are the main factors determining the pigment colour.

It must be also mentioned that the Mn-doped alumina pigments are industrially prepared by the traditional procedure, which involves the mixing of the metal cations precursors (hydroxides, oxides or carbonates) and the calcination at high temperature of the mixture to develop the pink colour and the corundum structure. Flux agents (alkaline halides or nitrates, borax, etc.), also called mineralizers, are also added, since it was reported that otherwise, a brownish black colour results which disappears after acidic washing leaving a white alumina powder.[2] However, we have recently shown that pink pigments can be also obtained after washing from Mn-alumina precursors prepared by using the pyrolysis of aerosols technique.[6] In this work, we have studied both kind of samples (prepared with and without fluxes) in order to elucidate the role that the flux agents play in the synthesis of this pigment. It should be noted that these additives might play a structural role as reported for other systems[7] although, in general, it is assumed that they increase the solid state reaction

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degree through the generation of a liquid phase which favours diffusion.

## 2. Experimental

### 2.1. Powders preparation

The composition of the studied samples (starting Mn/Al mol ratio = 0.05) was chosen within the optimum range previously reported for the commercial pigments (from ~0.03 to ~0.09).[8] For the preparation of the sample in the absence of fluxes through the pyrolysis technique, we used a procedure previously described, which can be summarised as follows.[6] A liquid aerosol was generated from an aqueous solution of aluminium(III) [$Al(NO_3)_3 \cdot 9H_2O$, Fluka, >99%] and manganese(II) [$Mn(NO_3)_2 \cdot 4H_2O$, Fluka, >97%] salts having a 0.5 mol $dm^{-3}$ $Al(NO_3)_3$ concentration and the required Mn/Al ratio, by using a commercial glass nozzle and air (0.5 kg $cm^{-2}$) as a carrier gas. The aerosol was then introduced into a furnace heated at 250 °C to evaporate the solvent from the droplets and finally into a second furnace at 600 °C, to decompose the metal precursors. The resulting solid particles were collected with a glass filter and further calcined at 900 °C for 3 h in a platinum crucible using a heating rate of 10 °C $min^{-1}$ to develop the corundum phase.

To prepare the sample by the traditional ceramic method in the presence of fluxes, we selected $Al(OH)_3$ (Riedel-de Haën, 99%) and $MnCO_3$ (Aldrich, 99.9%) as precursors, since as previously reported, the Mn–alumina solid solution can not be formed when starting from $\alpha$-$Al_2O_3$.[9] These precursors were mixed along with the mineralizers, 2.8 wt.% NaCl (Aldrich, 99%) and 2 wt.% NaF (Fluka, >99%), and the mixture was homogenised by gently milling in an agate mortar using acetone as dispersing medium before calcination at the 1050 °C for corundum crystallisation.

In all cases, the calcined samples were washed with an HCl (37%) hot solution to remove the unreacted phases. For this purpose, 300 mg of pigment were dispersed in 300 $cm^{-3}$ of the acid solution and kept for 3 h under stirring after which, they were centrifuged and washed with distilled water several times before drying at 50 °C.

### 2.2. Characterization

The composition of the powders (Mn/Al mol ratio) was determined by X-ray fluorescence (XRF, Siemens, SRS3000).

The crystalline phases present in the solids were identified by X-ray diffraction (XRD) (Siemens D501). Unit cell parameters were determined by a least squares refinement from the X-ray diffraction data collected at intervals of 0.02° ($2\theta$) for an accumulation time for interval of 10 seconds, using silicon (20% by weight) as internal standard. The crystallographic data for corundum ($\alpha$-$Al_2O_3$) were taken from its JCPDF file.[10]

The pigments colour was measured using a Dr. Lange, LUCI 100 colorimeter, for an illuminant D65 and a white tile ceramic (chromaticity coordinates: $x = 0.315$, $y = 0.335$) as standard reference. The colour was evaluated according to the Comission Internationale de l'Eclairage (CIE) by using $L^*a^*b^*$ parameters.[11] In this system, $L^*$ is the colour lightness ($L^* = 0$ for black and $L^* = 1$ for white), $a^*$ is the green (−)/red (+) axis, and $b^*$ is the blue (−)/yellow (+) axis.

X-ray photoelectron spectra (XPS) were obtained with a VG Escalab 210 model using the Mg$K_\alpha$ excitation source. Calibration of the spectra was done at the C1s peak of surface contamination taken at 284.6 eV. The peaks areas were corrected by the sensitivity factors of the elements as supplied by the instrument manufacturers.

The XANES and EXAFS spectra at the Mn K-edge (5989 eV) were measured at the BM29 beam line of the

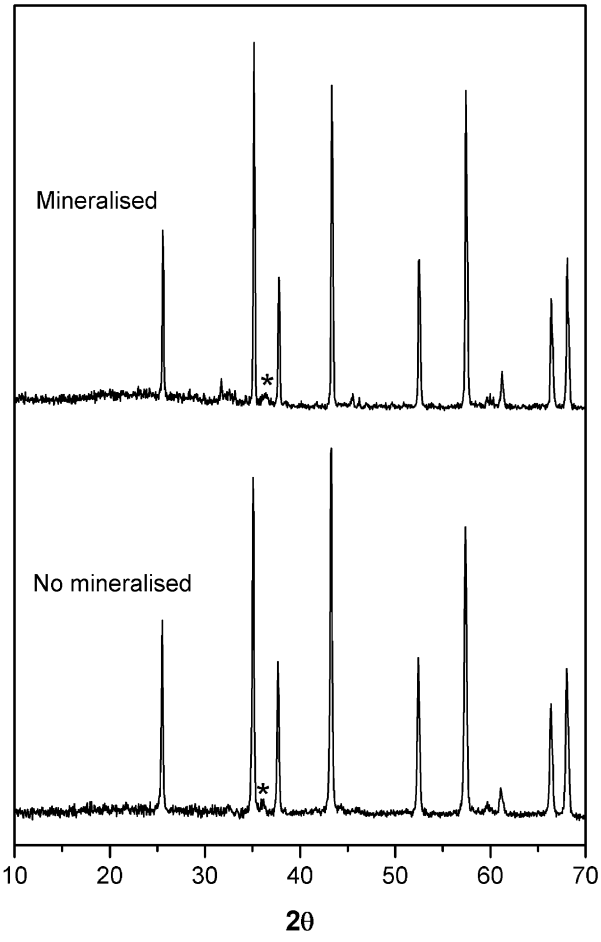


Fig. 1. X-ray diffraction patterns obtained before washing for the Mn-doped alumina pigments prepared in the absence and the presence of fluxes. The peaks corresponding to $Mn_3O_4$ have been labelled with an asterisk.

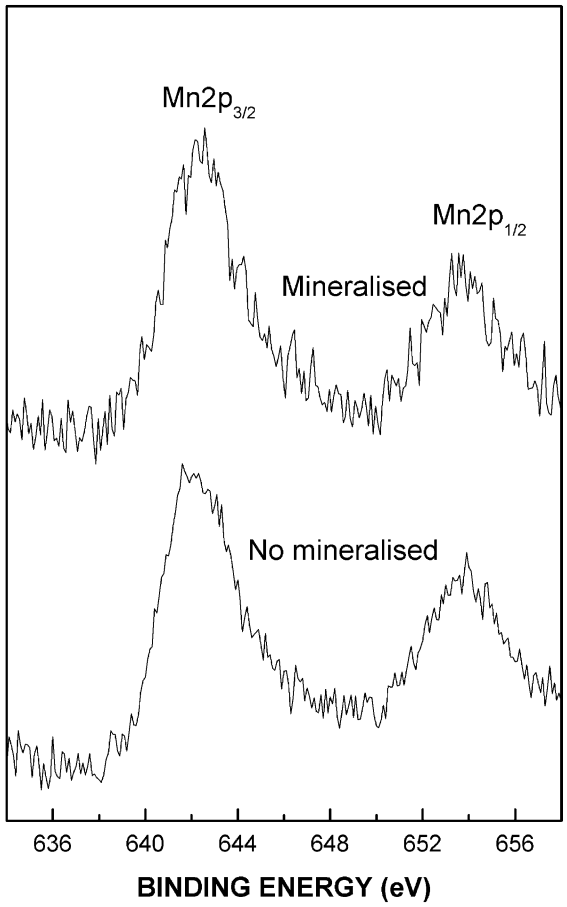


Fig. 2. XPS spectra obtained for the Mn-doped alumina washed samples prepared in the absence (no mineralised) and the presence (mineralised) of fluxes.

ESRF synchrotron facility (Grenoble, France) at room temperature in the transmission mode using two gas ionization chambers as detectors. Monochromatization of the light was done with a double-crystal monochromator [Si(111)]. The XANES spectra were mathematically treated in order to subtract the background absorption ($\mu_o$) coming from the other elements present in the samples and normalized. The experimental EXAFS data were analyzed with the software developed by Bonin et al.,[12] using the theoretical amplitude and phases shift functions proposed by Rehr et al. (version 6.01).[13] Mn(II) acetate, $Mn_2O_3$ and $MnO_2$ were used as a reference compounds. Theoretical FT curves were calculated by using the FEFF 7.0 ab initio code[14] assuming different compositions for the second coordination shell around the Mn cations. No Debye–Waller broadening was considered for these calculations.

## 3. Results and discussion

X-ray diffraction (Fig. 1) confirmed that both studied samples after calcination consisted of corundum ($\alpha$-$Al_2O_3$),[10] although in both cases, the pattern showed a weak reflection attributed to $Mn_3O_4$,[15] which disappeared after acidic washing (data not shown). This treatment obviously resulted in a decrease of the pigments Mn content, which was different depending on the preparation method. Thus, the resulting Mn/Al mol ratio was higher (0.035) for the mineralised sample than that for the one prepared in the absence of fluxes (0.021)

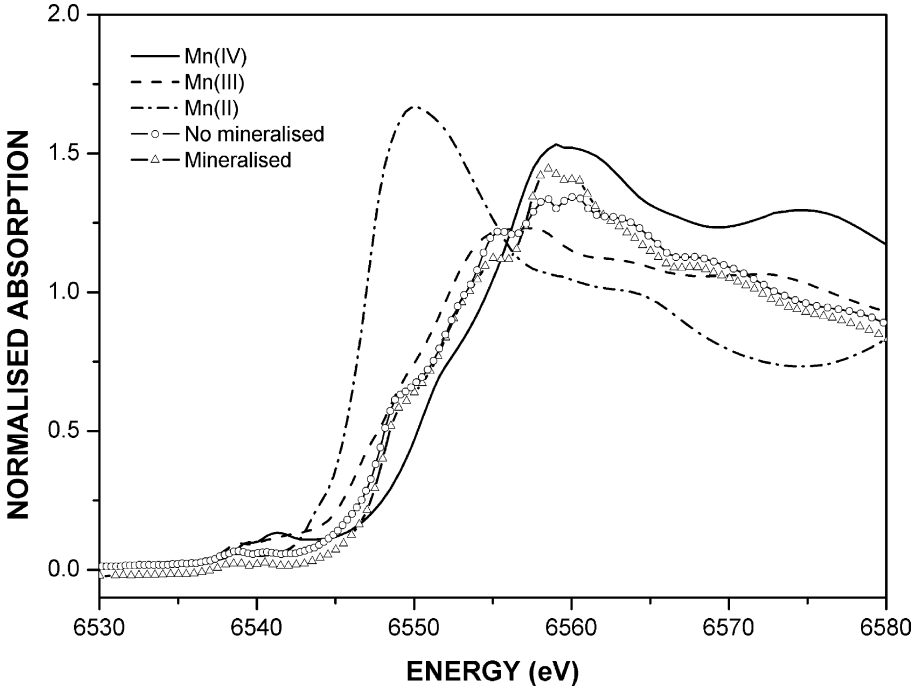


Fig. 3. XANES spectra at the Mn K-edge for the reference compounds and for the washed Mn-doped alumina samples prepared in the absence (no mineralised) and the presence (mineralised) of fluxes.

Table 1
Composition (Mn/Al mol ratio) measured by XRF and XPS, unit cell parameters (a, b and c), unit cell volume (V) and colour parameters ($L^*$, $a^*$, $b^*$) measured after washing for the Mn-doped alumina samples obtained in the absence (no mineralised) and the presence (mineralised) of fluxes. The unit cell parameters for an undoped alumina sample (blank) are also included

| | $(Mn/Al)_{XRF}$ mol ratio | $(Mn/Al)_{XPS}$ mol ratio | a and b/Å | c/Å | V/Å$^3$ | $L^*$ | $a^*$ | $b^*$ |
|---|---|---|---|---|---|---|---|---|
| Blank | | | 4.761 (1) | 12.999 (2) | 294.65 (17) | | | |
| No mineralised | 0.021 | 0.017 | 4.771 (1) | 13.019 (2) | 296.34 (17) | 65.9 | 11.0 | 4.8 |
| Mineralised | 0.035 | 0.013 | 4.773 (1) | 13.024 (3) | 296.70 (19) | 50.6 | 17.5 | 4.2 |

(Table 1). The formation of a Mn-corundum solid solution for both samples was evidenced by theirs unit cell parameters, which were higher than those for an alumina blank (Table 1), although the measured unit cell expansion was higher for the mineralised sample, in agreement with its higher Mn content (Table 1). This behaviour explains the redder (higher $a^*$) and more intense colour (lower $L^*$) observed for the sample prepared in the presence of fluxes (Table 1).

It should be noted that the unit cell expansion detected would be consistent with the presence in the solid solution of Mn(II) or Mn(III) cations since their ionic radius in octahedral coordination (0.67 and 0.58 Å, respectively) is higher than that of Al(III) (0.53 Å).[16] On the contrary, this result seems to discard the majority presence of Mn(IV), which should not induce appreciable changes in unit cell volume since its size (ionic radius = 0.54 Å)[16] is very similar to that of Al(III).

To gain more information on the oxidation state of the Mn cations, we first examined the XPS spectra of the samples finding that irrespective of the presence or absence of mineralization, the $Mn2p_{3/2}$ peak appeared at a binding energy of 642.1 eV for the washed samples (Fig. 2). This value was 1 eV higher than that expected for Mn(II) (640.9 eV)[17] suggesting a higher oxidation state, which was confirmed by the absence in the spectra of a satellite peak at a higher binding energy ($\Delta E \sim 6$ eV) characteristic of Mn(II) species.[17] However, its is outstanding that the observed $Mn2p_{3/2}$ peak position was intermediate between that reported for Mn(III) (641.8 eV) and Mn(IV) (642.5 eV).[17] Since the binding energy for these two species is very close and taking into account that XPS is basically a surface characterization technique, the analysis of the sample by bulk techniques such as XANES spectroscopy would be desirable for a more precise determination of the Mn chemical state. Nevertheless, the XPS spectra contained additional information regarding the distribution of the Mn cations in the alumina matrix. Thus, the Mn/Al mol ratio obtained from the areas of the Mn and Al peaks for the sample prepared in the absence of fluxes was very similar to that measured by X-ray fluorescence (Table 1), which may indicate that the Mn cations are homogeneously distributed within the alumina lattice. In the case of the mineralised sample such mol ratio was even lower than the overall value (Table 1) which could be due to the acidic washing treatment.

The XANES spectra at the K-edge for the no mineralised and mineralised samples are shown in Fig. 3 along with those for the references. As expected,[18] the main edge position obtained from the derivative spectra of the reference compounds was found to appear at higher energy as increasing the oxidation state (6544.7 eV for Mn(II), 6552 eV for Mn(III) and 6556.4 eV for

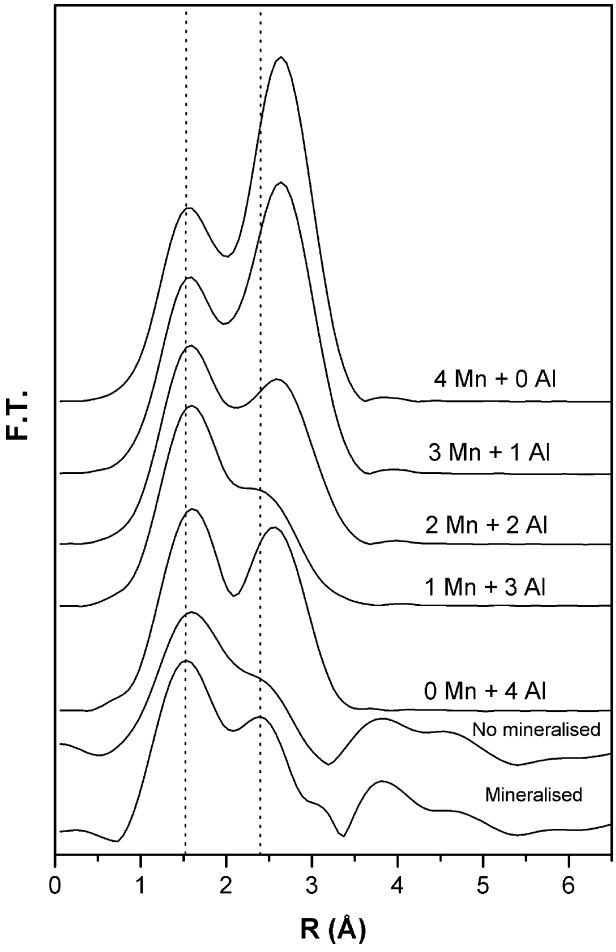


Fig. 4. F.T. functions obtained from the Mn K EXAFS oscillations of the washed Mn-doped alumina samples prepared in the absence (no mineralised) and the presence (mineralised) of fluxes. The F.T. curves calculated with the FEFF code for different compositions of the Mn second coordination shell in the corundum lattice are also included.

Mn(IV)). It was also observed that the spectra corresponding to both pigments were very similar showing the main edge at an intermediate position (6554 eV) between those of the Mn(III) and Mn(IV) references, although slightly closer to that of Mn(III). This finding was in agreement with the XPS observations, and in principle could be explained by the presence of a mixture of Mn(III) and Mn(IV) cations. However, this possibility seems unlikely since the observed spectrum could not be fitted by any combination of those of the Mn(III) and Mn(IV) references. In addition, the presence of an important amount of Mn(IV) in the corundum lattice must be disregarded in view of the observed unit cell expansion, as above discussed. Therefore, the presence of an oxidation state intermediate between Mn(III) and Mn(IV), which will be later interpreted, seems more reasonable.

The analysis of the EXAFS region of the XAS spectra gave additional information on the structural features of our pigments. The pseudo-radial distribution function (F.T. curve) at the Mn K edge uncorrected for the phase shift for no mineralised sample clearly showed the two first coordination shells around the Mn cations at 1.61 and ~2.38 Å (Fig. 4). The first one must correspond to the Mn-O bonds in the octahedral sites of the alumina lattice, whereas the second one, which in corundum is composed by four cations,[19] may consist of Al, Mn or Al/Mn mixtures. This complex situation makes difficult the fitting procedure of the EXAFS data. For this reason, theoretical F.T. curves were first calculated by using the FEFF code,[14] assuming all the possible compositions for the second shell (Fig. 4) in order to get an approximation to the identity of the present cations (Al and/or Mn). The comparison between the position and the relative intensity of the peak corresponding to this shell for the calculated and the experimental curves (Fig. 4) seems to suggest that such shell consists of 1 Mn and 3 Al cations, i.e. the Mn cations are ordered in the corundum lattice in the form of Mn–Mn pairs. Starting from this combination, the best fitting of the EXAFS data (Fig. 5) was then obtained for Mn–O (first shell), Mn–Al and Mn–Mn (second shell with Al/Mn ratio = 3) mean bond distances of 1.945, 2.801 and 2.889 Å, respectively. These distances are higher than those corresponding to Al–O (1.911 Å) and Al–Al (2.754 Å) bonds in the corundum lattice,[19] in agreement with the unit cell expansion observed for this pigment (Table 1), which must be induced by the formation of the Mn/$\alpha$–$Al_2O_3$ solid solution. These results may help to understand the features of the XANES spectrum of the pigment above discussed. Thus, the intermediate position observed for the main edge between those corresponding to the Mn(III) and Mn(IV) references may correspond to trivalent Mn, which in the alumina lattice would form Mn(III)–O bonds more ionic than those in $Mn_2O_3$ probably due to the presence in the Mn second coordination shell of the three Al(III) cations detected by EXAFS spectroscopy, which present a well known hard Lewis acid character.

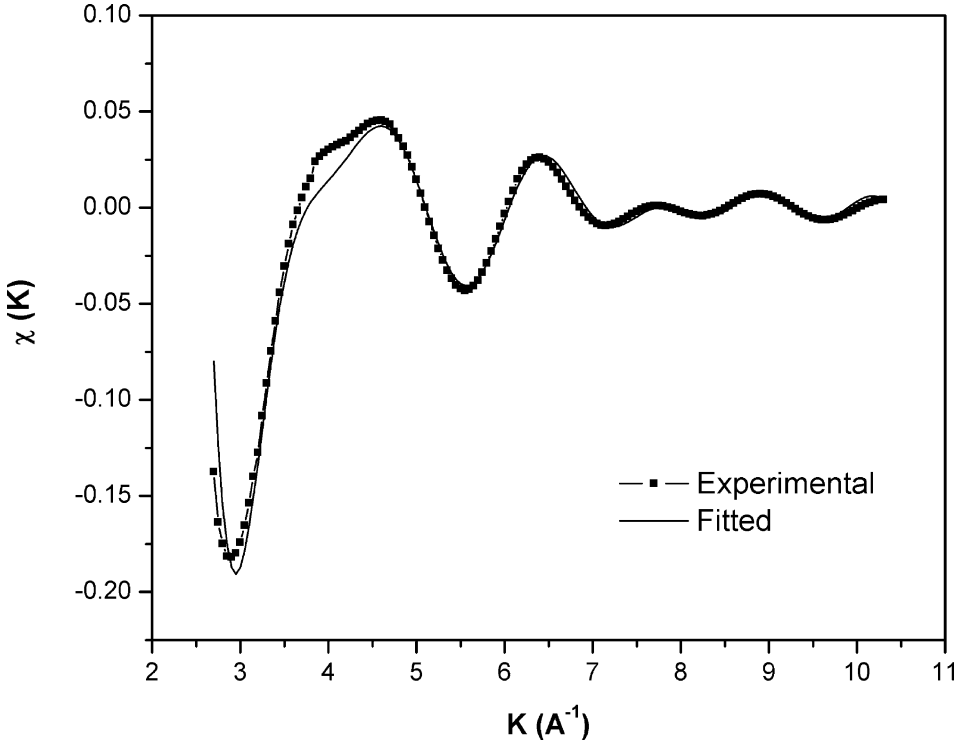


Fig. 5. Fitting analysis of the inverse F.T. curve obtained from the Mn K EXAFS oscillations of the sample prepared in the absence of fluxes.

The F.T. curve obtained for the mineralised sample was very similar to that of the one prepared in the absence of fluxes (Fig. 4), except that the peak corresponding to the second Mn coordination shell was slightly more intense for sample TF, suggesting that the composition of this shell was intermediate between that described by 1 Mn and 3 Al cations and by 2 Mn and 2 Al cations (Fig. 4). This finding was confirmed by the fitting of the experimental EXAFS curve for this sample, which was optimum for an Al/Mn ratio in this second shell slightly lower (2.85) than that for the no mineralised one (3.0). This behaviour can be related to the higher Mn content of the sample prepared in the presence of fluxes, which would induce a higher degree of Mn clustering. Since no other structural differences were found between the no mineralised and mineralised samples, we can conclude that the role that fluxes play in the preparation of the Mn-doped alumina pigments is to allow the incorporation of a higher amount of Mn(III) to the alumina solid solution by improving diffusion through the presence of a liquid phase. As a consequence, the pink colour was more intense and redder for the mineralised sample.

## 4. Conclusions

We have shown that irrespective of the addition of fluxes or not, the pink colour of Mn-doped corundum pigments is mainly due to Mn(III) species dissolved in the corundum lattice, which form clusters containing about 2 Mn cations with Mn–O bonds more ionic than those of Mn(III) oxide. The addition of fluxes yields redder and more intense colours due to the incorporation to the corundum lattice of a higher Mn amount, probably as a consequence of the generation of a liquid phase which favours the diffusion process involved in the solid solution formation.

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