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Aerosol-derived Mn-doped Al_2O_3 pink pigments prepared in the absence of fluxes

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Abstract

A method for the preparation of Mn-doped alumina pink pigments in the absence of fluxes through the pyrolysis of liquid aerosols generated from aluminium(III) nitrate and manganese(II) nitrate aqueous solutions is reported and compared with the traditional ceramic procedure. It was found that the pyrolysis method requires a lower temperature (900 °C) for the development of the corundum phase and the pink colour than that required by the traditional procedure (1300 °C) yielding a more intense colour, as a consequence of the incorporation of a higher amount of Mn in solid solution to the alumina lattice. In addition, the use of the pyrolysis procedure allows the preparation of pigments grains with uniform shape and controlled and reproducible size distribution, not requiring grinding.

Keywords: Alumina; Corundum; Manganese; Pigment; Pyrolysis

1. Introduction

Manganese-doped alumina (α-Al_2O_3) powders have important applications in the ceramic industry as pink pigments [1]. They are industrially produced by using the traditional ceramic procedure that involves the mixing of the metal cations precursors (hydroxides, oxides or carbonates) and the calcination at high temperature of the mixture to develop the desired colour and crystalline structure. Flux agents (alkaline halides or nitrates, borax, etc.), also called mineralizers, are also added to the starting mixture since they have been reported to be essential to promote the reaction between the Mn cations and alumina [2]. In general, this procedure also requires a final milling process to decrease the size of the pigments grains to the range 1–10 μm in which the ceramic pigments display their optimum characteristics (colour, chemical and colloidal stability, etc.) [3].

We have previously shown that the use of the spray pyrolysis technique for the synthesis of several pigment systems such as Cr–SnO_2 [4], Cr-$SnCaSiO_5$ [5] and Pr–CeO_2 [6], results in an important decrease of the calcination temperature required to develop the desired colours, for which, the use of the fluxes involved in the traditional method is not need. In addition, powders with controlled particle size and shape can be so obtained, without the need for the grinding

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Table 1
Composition (Mn/Al atomic ratio), 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 by different procedures and heated at different temperatures (the Mn/Al atomic ratio before washing (nominal) is also included)

Synthesis method	$(Mn/Al)_{nominal}$ atomic ratio	$(Mn/Al)_{XRF}$ atomic ratio	*a* and *b* (Å)	*c* (Å)	*V* (Å^3)	L^*	a^*	b^*
Pyrolysis/1300 °C	0		4.761 (1)	12.999 (2)	294.65 (17)			
Pyrolysis/900 °C	0.05	0.021	4.771 (1)	13.019 (2)	296.34 (17)	65.9	11.0	4.8
Pyrolysis/1100 °C	0.05	0.015	4.766 (1)	13.010 (2)	295.52 (17)	69.6	10.8	4.6
Pyrolysis/1300 °C	0.05	0.011	4.766 (1)	13.011 (2)	295.54 (17)	72.2	11.2	4.2
Pyrolysis/1100 °C	0.01	0.010	4.764 (1)	13.006 (1)	295.18 (15)	70.1	10.1	5.0
Pyrolysis/1100 °C	0.20	0.021	4.768 (1)	13.017 (2)	295.92 (17)	65.9	10.5	4.6
Traditional/1300 °C	0.05	0.010	4.763 (1)	13.007 (1)	295.08 (14)	72.3	10.4	4.3

process involved in the traditional method. Finally, this method is continuous, which is preferred for industrial purposes.

In this paper, we explore the applicability of the spray pyrolysis method to the preparation of Mn-doped alumina pink pigments in the absence of fluxes. Since this procedure produces amorphous powders, the structural, morphological and compositional changes originated during their thermal treatment were studied in detail. Finally, the manganese content of the samples was systematically varied in order to optimise the pigment resulting from this procedure.

2. Experimental

2.1. Materials

Aluminium nitrate [$Al(NO_3)_3 \cdot 9H_2O$, Fluka, >99%], manganese(II) nitrate [$Mn(NO_3)_2 \cdot 4H_2O$, Fluka, >97%], aluminium hydroxide [$Al(OH)_3$, Riedel-de Haën, 99%], manganese(II) carbonate ($MnCO_3$, Aldrich, 99.9%) and hydrochloric acid (Aldrich, 37%) were used as received.

2.2. Powders preparation

For the preparation of the samples by the pyrolysis technique, liquid aerosols generated from aqueous solutions of aluminium(III) and manganese(II) nitrates were thermally decomposed in an

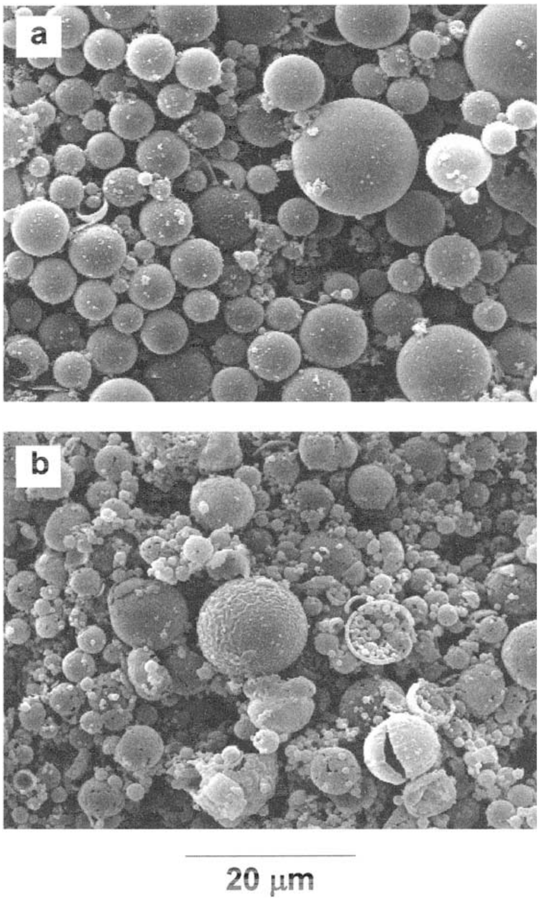

Fig. 1. SEM micrographs of the Mn-doped alumina sample prepared by pyrolysis of aerosols (starting Mn/Al atomic ratio = 0.05) as prepared (a) and after heating at 1300 °C (b).

apparatus previously described [5]. Essentially, the procedure was as follows. The starting solutions having a constant $Al(NO_3)_3$ concentration (0.5 mol dm^{-3}) and the $Mn(NO_3)_2$ amount required to give the desired Mn/Al atomic ratio, were first atomized using a commercial glass nozzle and air (0.5 kg cm^{-2}) as a carrier gas. The resulting 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 yielding solid particles, which were finally collected with a glass filter. To develop the corundum phase and pink colour, these powders were further calcined at different temperatures for 3 h in platinum crucibles using a furnace which was heated up to the selected temperature at a heating rate of 10 °C min^{-1}. The Mn/Al atomic ratio was varied from 0.01 to 0.2 (Table 1) in order to analyse the influence of the chromophore (Mn) content on the pigments colour properties.

For comparison purposes, we also studied a sample prepared by the traditional ceramic method in the absence of fluxes using $Al(OH)_3$ and $MnCO_3$ (Mn/Al atomic ratio of 0.05) as precursors [2], which were mixed and homogenised by gently milling in an agate mortar using acetone as dispersing medium before calcination at the minimum temperature required for corundum crystallisation.

To remove the unreacted phases, all calcined samples were washed with a hot solution of HCl (37%) by dispersing 300 mg of pigment in 300 cm^{-3} of the acid solution. The dispersions were stirred for 3 h, then centrifuged and the powders

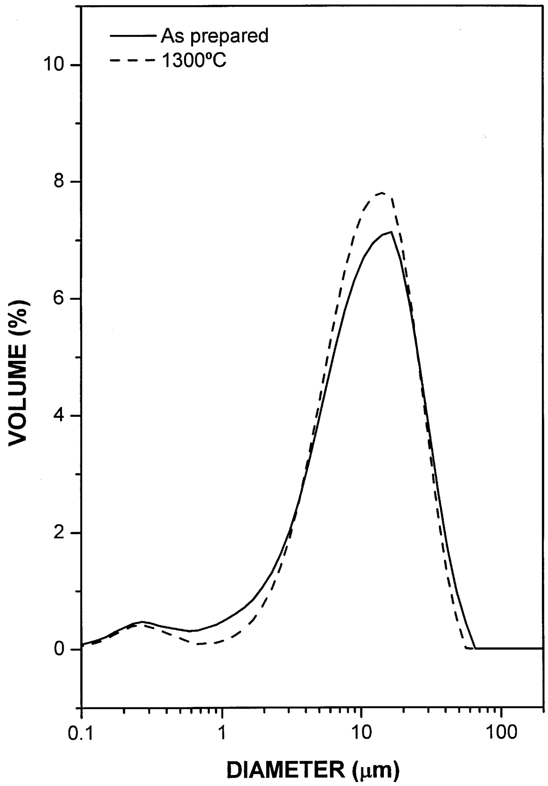

Fig. 2. Volumetric particle size distribution of the Mn-doped alumina samples shown in Fig. 1.

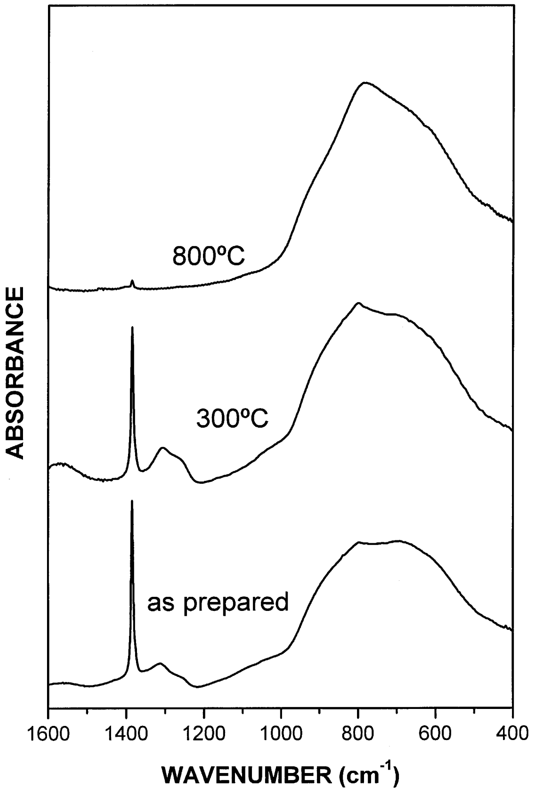

Fig. 3. Infrared spectra of the Mn-doped alumina sample prepared by pyrolysis of aerosols (starting Mn/Al atomic ratio = 0.05) as prepared and after heating at different temperatures under the DTA/TGA conditions.

washed with distilled water several times before drying at 50 °C.

2.3. Characterization

The particle size and shape of the powders were examined by scanning electron microscopy (SEM, Jeol JSM5400). The volumetric particle size distribution of the samples was obtained from laser diffraction measurements (Malvern Mastersizer S). The composition of the powders (Mn/Al atomic ratio) was determined by X-ray fluorescence (XRF, Siemens, SRS3000).

The infrared spectra for the powders diluted in KBr pellets were recorded in a Nicolet 510 Fourier transform spectrometer. Differential thermal (DTA) and thermogravimetric (TGA) analyses (Seiko, EXSTAR 6000) were carried out in air at a heating rate of 10 °C min^{-1}.

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° (2θ) for an accumulation time for interval of 10 s, using silicon (20% by weight) as internal standard. The crystallographic data for corundum (α-Al_2O_3) were taken from Ref. [7].

The colour of the pigments was evaluated according to the Comission Internationale de l'Eclairage (CIE) by using $L^*a^*b^*$ parameters [8]. 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. These parameters were obtained with a Dr. Lange (LUCI 100) colorimeter, using a D65 illuminant and a white tile ceramic (chromaticity coordinates: $x=0.315$, $y=0.335$) as standard reference. The measurements were conducted on the powdered samples contained in a quartz cell.

3. Results and discussion

The composition of the first studied sample (starting Mn/Al atomic ratio = 0.05, Table 1) was chosen within the optimum range previously reported for the commercial pigments (from ~0.03 to ~0.09) [9]. The powder with this nominal composition produced by the aerosol procedure consisted of spherical particles of heterogeneous size (Fig. 1a) showing two maxima at ~0.25

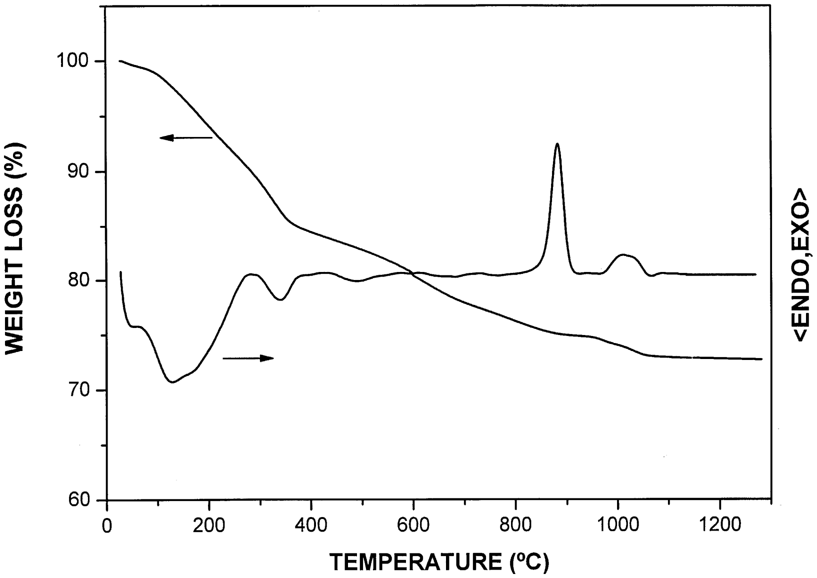

Fig. 4. Differential thermal and thermogravimetric curves obtained for the Mn-doped alumina sample prepared by pyrolysis of aerosols (starting Mn/Al atomic ratio = 0.05).

(weak) and ~15 μm (more intense) in the volumetric size–distribution curve (Fig. 2). These particles were amorphous to X-ray diffraction and contained a certain amount of nitrate anions coming from the incomplete decomposition of the metal salts, as indicated [10] by a band at 1385 cm^{-1} appearing in their infrared spectrum (Fig. 3). This spectrum also displays a much weaker absorption at 1315 cm^{-1} suggesting the presence of some adsorbed carbonate anions [10].

The DTA and TGA curves obtained for this sample are shown in Fig. 4. As observed, a strong and broad endothermic feature was detected between 25 and 250 °C due to the release of adsorbed water (~10% by weight). Two weaker endothermic peaks centred at 335 and 490 °C were also observed accompanied by a continuous weight loss (~15%) between 250 and 800 °C, which can be mainly ascribed to the decomposition of the unreacted nitrate anions and the adsorbed carbonates, as indicated by the disappearance of the bands at 1385 and 1315 cm^{-1} in the infrared spectrum of the sample heated at 800 °C (Fig. 3). Finally, two exothermic effects were detected at 885 and 1010 °C, respectively. As supported by the X-ray diffraction patterns of the sample heated at 900 and 1100 °C under the non isothermal conditions used for the thermal analyses (Fig. 5), the first one can be associated with the crystallization of η-Al_2O_3 [11], whereas the latter corresponds to the transformation of this phase to corundum (α-Al_2O_3) [7]. A small weight loss (~2%) was also detected in this temperature range, which could be tentatively ascribed to the release as water of some residual OH groups. It should be noted that formation of the corundum phase occurred in this sample at lower temperature than that required (1180 °C) for an undoped alumina sample (blank) prepared by a similar procedure (Fig. 6). Such a decrease seems to be associated to the presence of Mn, since it was more considerable as the Mn/Al ratio of the doped samples increased (Fig. 6).

The isothermal treatment for 3 h of the sample resulted in a further decrease of the temperature required for the full development of the corundum phase to 900 °C, as revealed by X-ray diffraction (Fig. 7). The pattern obtained after this treatment also showed the presence of a weak reflection at $2\theta \sim 35.9$, attributed to a manganese spinel (Mn_3O_4) [12], which was still detected after heating at higher temperatures up to 1300 °C (Fig. 7). Because of this phase, this pigment did not present the pink colour characteristic of Mn-doped corundum; instead a brown colour was observed after calcination in this temperature range. According to X-ray diffraction (data not shown), such spinel phase could be removed by washing the heated samples with hot concentrated HCl. A pink colour then appeared characterised by *a** and *b** parameters whose values did not change significantly with increasing the heating temperature (Table 1). However, this treatment gave rise to an increase of the colour lightness (*L**), which can be explained by the decrease of the amount of Mn retained in the sample detected after washing (from 0.021 to

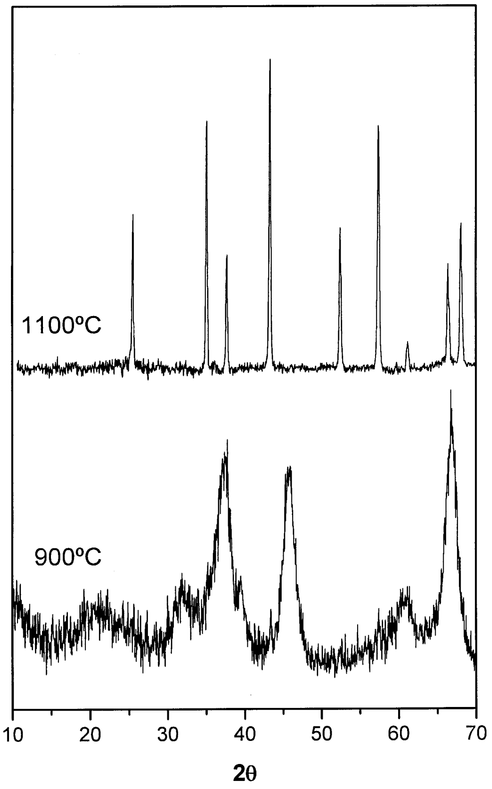

Fig. 5. X-ray diffraction patterns obtained for the Mn-doped alumina sample prepared by pyrolysis of aerosols (starting Mn/Al atomic ratio = 0.05) after heating at different temperatures under the DTA/TGA conditions.

0.011) as the temperature was raised from 900 to 1300 °C (Table 1). An expansion of the corundum unit cell was also detected for all samples (Table 1), which was less significant as the heating temperature increased, in agreement with the decrease of the Mn content. This finding revealed that, as suggested [2], the formation of a solid solution between the Mn cations and the corundum lattice is responsible for the pink colour and probably for the catalytic effect of Mn doping on the corundum formation above mentioned. The observed decrease of the Mn amount in solid solution with increasing the calcination temperature can be explained if we assume a trivalent oxidation state for Mn [2]. It is well known that Mn(III) oxide is produced when Mn(II) compounds or the Mn_3O_4 spinel are heated in the 500–950 °C range and becomes unstable at higher temperature yielding Mn_3O_4 [13]. Therefore, the relative amount of Mn(III) available for the formation of the Mn(III)–Al_2O_3 solid solution must decrease as increasing temperature above 950 °C.

For comparison, a Mn-doped alumina sample was also prepared with the same Mn/Al ratio of the above one by using the traditional ceramic procedure. As precursors we used $Al(OH)_3$ and $MnCO_3$, since as previously reported [14], no Mn-alumina solid solution can be formed when starting from α-Al_2O_3. Under these conditions, it was found that the temperature required for the full development of corundum was much higher (1300 °C) (Fig. 7) than that involved in the pyrolysis procedure (900 °C). The sample prepared by the traditional method also contained a certain amount of Mn_3O_4 (Fig. 7) which could be completely removed by HCl washing, resulting in a Mn/Al ratio and a pink colour similar to those corresponding to the sample obtained by our procedure when heated at the same temperature (1300 °C) (Table 1). Therefore, the main advantage of the newly developed procedure is that it permits the preparation of Mn-doped α-Al_2O_3 pink pigments in the absence of fluxes at a much lower temperature (900 °C) than that required by the traditional ceramic procedure (1300 °C), yielding more intense colours, since the amount of Mn incorporated to the corundum lattice increased with decreasing preparation temperature. In addition, the pigments obtained by our procedure do not require grinding and consist of grains with

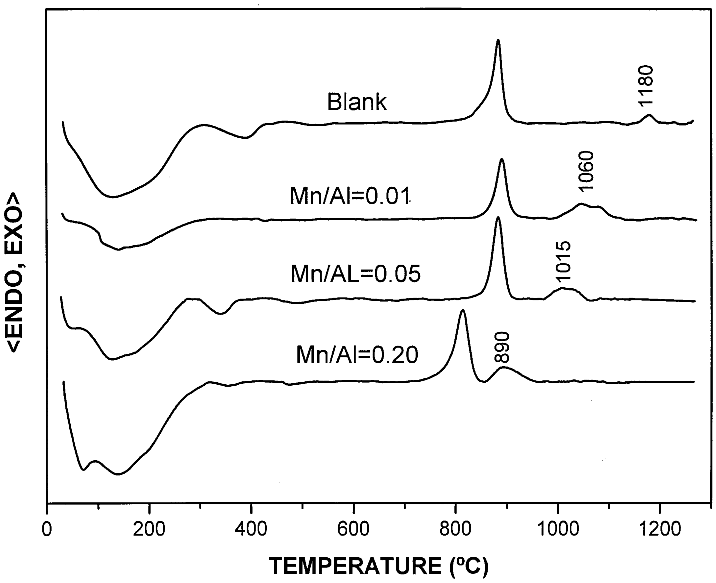

Fig. 6. Differential thermal analysis obtained for several Mn-doped alumina samples prepared by pyrolysis of aerosols with different starting Mn/Al atomic ratio and for the alumina blank.

controlled and reproducible size distribution and uniform shape, since after calcination, the spherical shape was retained (Fig. 1b). It should be noted that these spherical grains were polycrystalline (Fig. 1b) and that the mean size of the spheres was not significantly reduced after heating (Fig. 2) in spite of the weight losses detected by TGA (Fig. 4).

Because of the high Mn losses (~60%) detected during the washing procedure (Table 1), the starting Mn/Al ratio was varied from 0.01 to 0.20, in order to optimize the preparation procedure and colour. These powders were heated at 1100 °C, as the sample with less Mn content did not completely form corundum at lower temperatures (Fig. 6). It should be noted that when decreasing the raw Mn/Al atomic ratio from 0.05 to 0.01, only the patterns of corundum were detected by X-ray diffraction in the unwashed sample (data not shown), for which the washing treatment was not carried out in this case. As expected from the slightly lower Mn content of this pigment when compared with that of the former sample (Mn/Al atomic ratio after washing = 0.015) (Table 1), its corresponding unit cell expansion was also slightly lower (Table 1). However, these small differences in Mn content did not result in appreciable changes in the $L^*a^*b^*$ parameters and therefore, in colour (Table 1). It was also found that the increase of the starting Mn/Al ratio from 0.05 up to 0.2, did not give rise to any significant increase of the amount of Mn retained after washing (Mn/Al increased from 0.015 to 0.021) (Table 1), since most (90%) of the Mn initially added was removed by leaching. In agreement, the differences in the unit cell expansion and colour for both samples were very small. In fact, only a slight decrease of lightness (L^*) was observed for the most Mn concentrated sample (starting Mn/Al ratio = 0.2), whose $L^*a^*b^*$ parameters were very similar to those of the sample prepared from a lower raw Mn/Al ratio = 0.05, heated at 900 °C (Table 1). Therefore, the latter sample can be considered as the optimum pigment since it shows the best colour parameters (lower lightness, L^*, and higher red parameter, a^*) with the minimum amount of Mn after calcination at the lowest temperature.

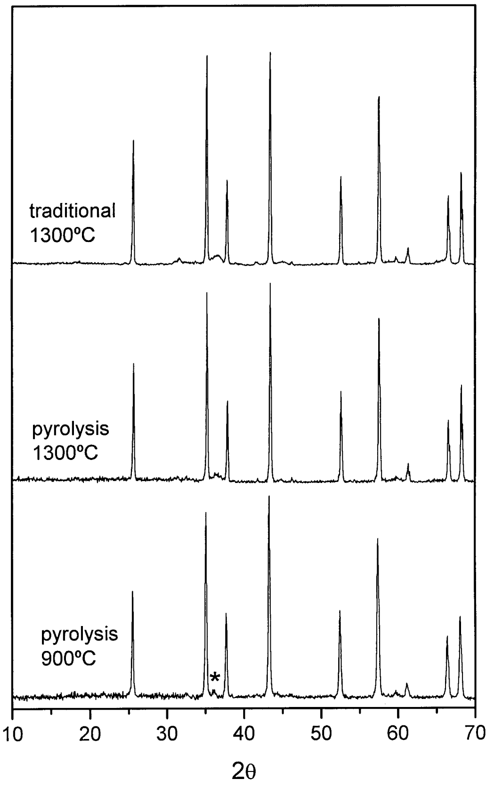

Fig. 7. X-ray diffraction patterns obtained for the Mn-doped alumina sample prepared by pyrolysis of aerosols (starting Mn/Al atomic ratio = 0.05) after heating for 3 h at different temperatures and for a sample with the same starting Mn/Al ratio prepared at 1300 °C by the traditional method in the absence of fluxes (Table 1). The peaks corresponding to Mn_3O_4 have been labelled with an asterisk.

4. Conclusions

We have shown that the use of the pyrolysis of aerosols procedure has enables us to prepare Mn-doped alumina pink pigments in the absence of fluxes at lower temperature (900 °C) than that required by the traditional method (1300 °C). In addition, the amount of Mn incorporated in solid solution to the alumina matrix was higher in the aerosol-derived pigments, which consequently resulted in a more intense colour. Finally, the pyrolysis method yields powders with controlled particle size and spherical shape, not requiring the grinding process involved in the traditional procedure.

Acknowledgements

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