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Preparation and Sintering Behaviour of Ultrafine Mn/Fe and Fe/Co Mixed Oxides

J. M. Jiménez-Mateos, J. Morales & J. L. Tirado

Departamento de Química Inorgánica e Ingeniería Química, Facultad de Ciencias, Universidad de Córdoba,
14004 Córdoba, Spain

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Abstract

Mn/Fe and Fe/Co mixed oxides with spinel structures were prepared by low-temperature (300–400°C) thermal decomposition of carbonate precursors. The oxide samples are cation-deficient phases with average oxidation state of the metal ions of ca. *3·0, and consist of fine particles (*ca. *10 nm) which are single crystalline domains with few lattice distortions. Gas adsorption measurements reveal values of specific surface area between 30 and 120* $m^2 g^{-1}$ *and the presence of an interparticle porous system. Pelletized aggregates of selected compositions sinter to almost theoretical densities at 1000°C and release oxygen excess from the spinel structure. The sintered pellets show little intergranular porosity.*

Ausgehend von Carbonaten wurden Mn/Fe- und Fe/Co-Mischoxide mit Spinellstruktur durch thermische Zersetzung bei niedrigen Temperaturen (300–400°C) hergestellt. Die Oxide weisen einen Kationenmangel (mit einem durchschnittlichen Oxidationszustand der Metallionen von ca. *3·0) auf und bestehen aus feinen einkristallinen Partikeln (etwa 10 nm), die wenige Gitterstörungen aufweisen. Die spezifischen Oberflächen der Pulver wurden durch Gasadsorptionsmessung bestimmt und liegen zwischen 30 und 120* $m^2 g^{-1}$*, was auf ein Interpartikel-Porensystem hinweist. Pelletierte Aggregate ausgewählter Zusammensetzungen sintern bei 1000°C fast bis zur theoretischen Dichte, wobei der Sauerstoffüberschuß aus der Spinellstruktur abgegeben wird. Die gesinterten Tabletten zeigen nur eine geringe intergranulare Porosität.*

Des oxydes mixtes de Mn/Fe et Fe/Co de structure spinelle ont été synthétisés à partir de la décomposition à basse température de précurseurs carbonates entre 300 et 400°C. Les oxydes obtenus présentent des déficiences cationiques avec un état d'oxydation moyen des cations de 3·0, et ils forment de petites particles (10 nm) qui sont des domaines monocristallins de maille peu déformée. Les mesures par adsorption de gaz donnent des valeurs de surface spécifique comprises entre 30 et 120 $m^2 g^{-1}$ *et révèlent la présence d'une porosité interparticulaire. Des compacts préparés à partir de mélanges de compositions selectionnées ont été frittés à 1000°C, avec dégagement de l'excès d'oxygène contenu dans la structure spinelle. Les valeurs de densité obtenues sont proches de la valeur théorique. Les compacts frittés montrent peu de porosité intergranulaire.*

1 Introduction

In the preparation of transition-metal ferrites by the conventional ceramic procedure it is often found that some morphological parameters such as particle size and shape are important factors that determine the rate and extent of the reactions and the reproducibility of the final properties of the products. In this way, different procedures have been developed to obtain ceramic oxides with controlled composition homogeneity by reducing the chemical diffusion distances during the preparation reactions. These include the wet method—coprecipitation and oxidation reactions[1–4]—and the low-temperature decomposition of adequate precursor compounds—including phases as oxalates,[5,6] carbonates,[7,8] hydroxinitrates,[9] hydrazinecarboxilate hydrates[10] and organometallic polymers.[11] Both synthetic

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variants usually lead to ultrafine materials, with particle sizes that can be close to some ten times the unit cell parameters of the solid.

On the other hand, the ceramic interest of these highly-dispersed materials is also connected with their sintering behaviour. Thus, nearly theoretical densities have been achieved by sintering ultrafine, ferrite particles obtained by the wet method.[4] This paper reports a study on the applicability of mixed carbonate precursors in the preparation of ultrafine Mn/Fe and Fe/Co mixed spinel oxides with suitable chemical properties and sintering behaviour. The startpoint of this study is the fact that Mn, Fe and Co carbonates crystallize with a calcite structure and can be prepared over a wide compositional range of solid solutions. These precursors have been previously used in the preparation of new[7] and metastable modifications of mixed transition metal oxides.[12]

2 Experimental

Mixed Mn/Fe and Fe/Co carbonates were prepared by direct precipitation from divalent metal solutions with 1 M HCO_3^- while continuously passing CO_2.[7] The thermal decomposition processes of the mixed carbonates was followed by Differential Scanning Calorimetry (DSC) with a Mettler TA3000 apparatus. Thermally decomposed samples were obtained after 1 h of isothermal treatment of the carbonate samples at 300 and 400°C for the Co/Fe and Mn/Fe systems, respectively. Iron to total metal ratios (Fe/M) were determined by atomic absorption spectrometry while composition homogeneity was tested by ED X-ray electron microprobe measurements. The average oxidation state of metal ions in the oxide samples was determined after dissolution of the solid in the presence of Fe(II) in an inert atmosphere and by back-titrating with standard $K_2Cr_2O_7$, according to a published procedure.[12]

Powder X-ray diffraction patterns were obtained with a Siemens 501 diffractometer provided with CuK_α radiation and graphite monochromator. Si and Co_3O_4 were used as standards in the determination of unit cell parameters and line broadening analysis. Single-line broadening analysis was carried out by profile fitting to Pearson-VII functions.[13] After correction for the instrumental broadening, crystallite size and microstrains were computed from the Cauchy and Gauss components of the pure profile integral breadths. Transmission electron micrographs were obtained with a JEOL 200 CX apparatus. N_2 adsorption–desorption isotherms were obtained in a conventional volumetric apparatus. The dead spaces were calibrated with He gas.

The sintering behaviour was followed for two samples of selected compositions that were mixed with 1% polyvinyl alcohol, pelletized and sintered at 600°C for 1·5 h and 1000°C for 1·5 h. The apparent density of the sintered pellets was determined by the conventional Archimedes procedure. Scanning electron micrographs were obtained with a Philips SEM 501 B apparatus.

3 Results and Discussion

The mixed Mn/Fe and Fe/Co carbonates were obtained as powdered monophasic solids with a calcite structure, as shown by X-ray diffraction. Particle size was close to 5 μm and a high homogeneity of cation distribution was observed from electron microprobe measurements. The various Fe/M ratios determined by atomic absorption spectrometry in the carbonate samples that were coincident with the values of the products of their thermal decomposition are shown in Table 1. The precursor method allows the preparation of mixed phases in the complete compositional range.

The DSC traces of the carbonate samples recorded under static air atmosphere are included in Fig. 1. These curves show a complex endothermal effect that can be ascribed to carbonate decomposition. The decomposition temperatures are low (between 300 and 400°C) in the Mn/Fe and Fe/Co systems although peak temperature increases progressively with the substitution of Fe by Mn and Co, according to previous work.[14] Nevertheless, the temperatures are sufficiently low to inhibit simultaneous sintering processes of the reaction products. The complex decomposition endotherms of Fig. 1 are followed by exothermal effects of variable intensity. This effect occurs at lower temperatures for Co-containing samples (Fig. 1, a–c) and is more marked for Mn-containing products. On the other hand, the effect was not shown in the DSC traces recorded under a dynamic Ar atmosphere. The exotherm can be ascribed to oxidation phenomena of the initial products of decomposition of the divalent-metal carbonates, due to the presence of O_2 in the reaction medium. However, the contribution of partial oxidation by CO_2 cannot be discounted, on the basis of previous research.[14]

Due to the above described oxidation processes, the products of isothermal treatment during 1 h at 300 and 400°C for the Fe/Co and Mn/Fe systems, respectively were cation-deficient spinel oxide

Table 1. Chemical composition, structural parameters and specific surface area of mixed Mn/Fe and Fe/Co spinel oxides

System	*Fe/M*	*O/M*	*a(nm)*	$S_{BET}(m^2 g^{-1})$	$D_{220}(nm)$	$\tilde{e}_{220}$ (10^3)
Co, Fe prepared at 300°C	0·857	1·433	$0{\cdot}836\,5_7$	54	9·8	0·00
	0·684	1·380	$0{\cdot}837\,5_9$	40	9·9	0·00
	0·623	1·382	$0{\cdot}837\,6_4$	56	8·7	1·27
	0·467	1·372	$0{\cdot}824\,3_7$	118	6·5	14·05
	0·396	1·359	$0{\cdot}820\,3_2$	61	7·8	14·97
	0·354	1·354	$0{\cdot}820\,0_8$	75	9·6	9·45
	0·153	1·336	$0{\cdot}813\,2_5$	76	9·9	2·32
	0·000	1·333	$0{\cdot}806\,9_8$	40	24·7	5·11
Mn, Fe prepared at 400°C	0·856	1·569	$0{\cdot}836\,4_6$	53	23·5	3·11
	0·650	1·607	$0{\cdot}837\,6_4$	71	12·6	0·86
	0·577	1·600	$0{\cdot}839\,6_5$	60	10·3	4·34
	0·502	1·593	$0{\cdot}843\,4_3$	64	11·1	6·02
	0·360	1·599	$0{\cdot}844\,2_0$	90	12·3	7·18
	0·330	1·609	$0{\cdot}844\,8_0$[a]	40	13·6	7·85
	0·134	1·600	[b]	37	—	—
	0·000	1·600	[b]	27	—	—

S_{BET}, BET surface; D,'crystallite size; $\tilde{e}$, microstrain content.

[a] Pseudocubic phase.

[b] Tetragonal phases.

phases (Fig. 2). The average oxidation states of the metal ions in the samples shown in Table 1 agree with the presence of cation vacancies in the spinel structure, as the O/M ratio is higher than 1·33 (corresponding to a M_3O_4 stoichiometry). Values of the O/M ratio higher than 1·5 (corresponding to a M_2O_3 stoichiometry) were found for Mn-containing samples and indicate the presence of Fe(III), Mn(III) and Mn(IV) in the oxides.

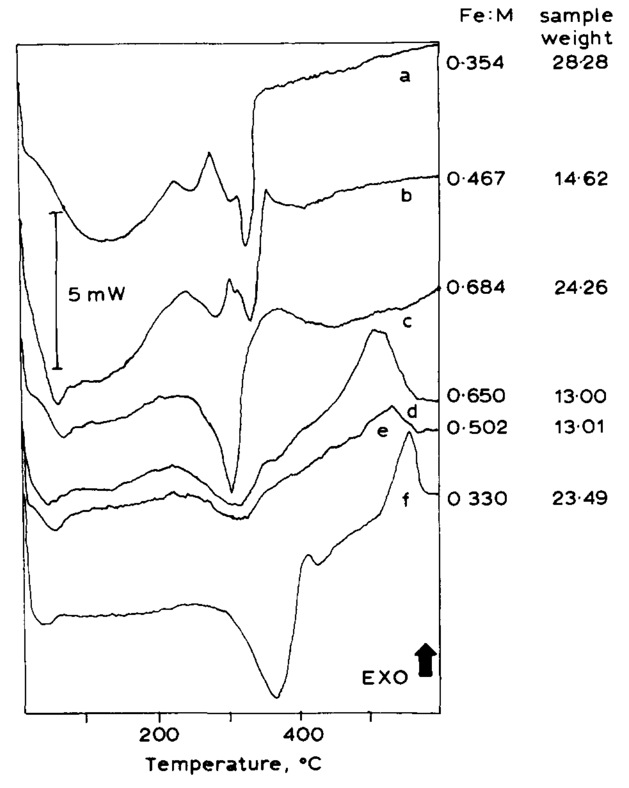
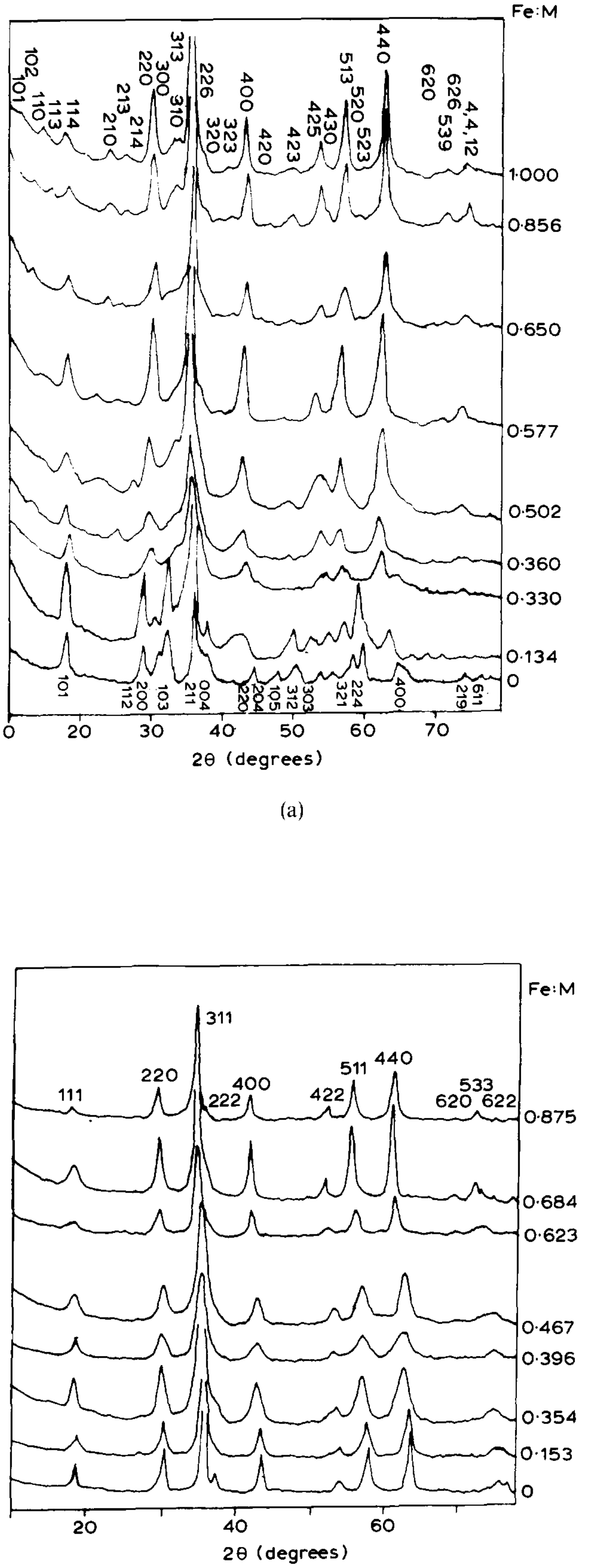


Fig. 1. DSC traces of selected samples of mixed Fe/Co (a–c) and Fe/Mn (d–f) carbonates.

According to the X-ray diffraction data in Fig. 2, the spinel oxides are cubic phases except for Mn-containing samples with Fe/(Fe + Mn) ratios below 0·33. These samples showed a tetragonal spinel structure similar to that of Mn_3O_4, due to the effect of the Jahn–Teller distortion of the octahedrally coordinated Mn(III) ions (see Fig. 2(a)). On the other hand, Fe-rich samples showed the presence of extra lines in the XRD patterns (Fig. 2) that are ascribable to a tetragonal superstructure similar to that of γ-Fe_2O_3. This fact is in agreement with the significant level of cation vacancies in the structure of the solids.

In connection with the unit cell parameters of cobalt ferrites, it should be noted that previous studies[1,15] have shown a direct effect of the method of preparation and particle size on these parameters. According to Burriesci *et al.*[15] those samples prepared by ceramic methods exhibit lower *a* values than samples prepared by wet procedures. The values of this parameter shown in Table 1 are closer to those expected for ceramic samples. This could be initially ascribed to a particle size of the ex-carbonate samples higher than that found in samples prepared by direct precipitation. However, the results of the evaluation of N_2 adsorption isotherms (Fig. 3), transmission electron microscopy (Fig. 4) and XRD line broadening analysis (Table 1) do not support this assumption.

Thus, the values of BET surface shown in Table 1 are somewhat high and hence indicative of high sample dispersion. In addition, Fig. 4 reveals a small



(a)

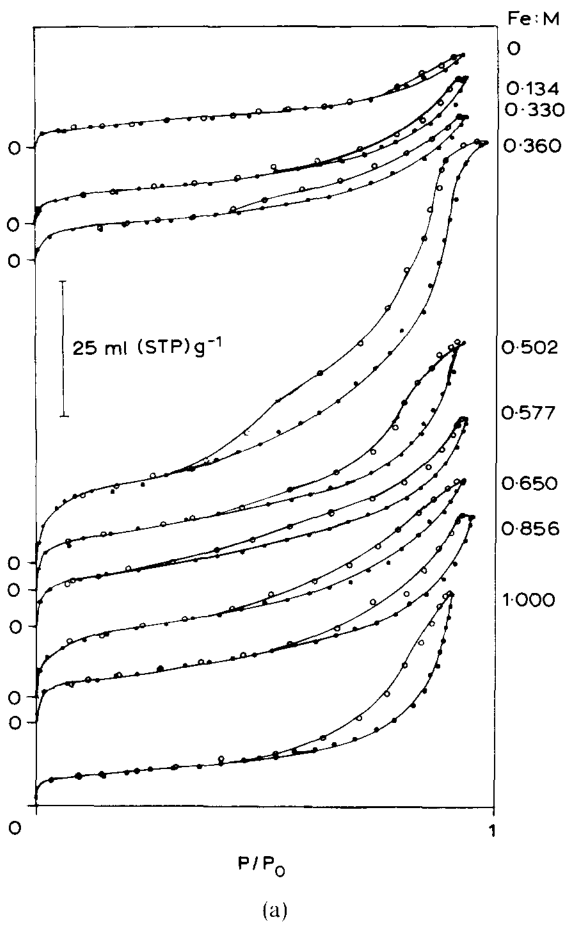
(b)

Fig. 2. X-ray diffraction patterns of mixed Mn/Fe carbonates decomposed at 400°C (a) and mixed Fe/Co carbonates decomposed at 300°C (b). Upper Miller indices in (a) correspond to γ-Fe_2O_3 and lower indices to γ-Mn_2O_3; indices in (b) to Co_3O_4.

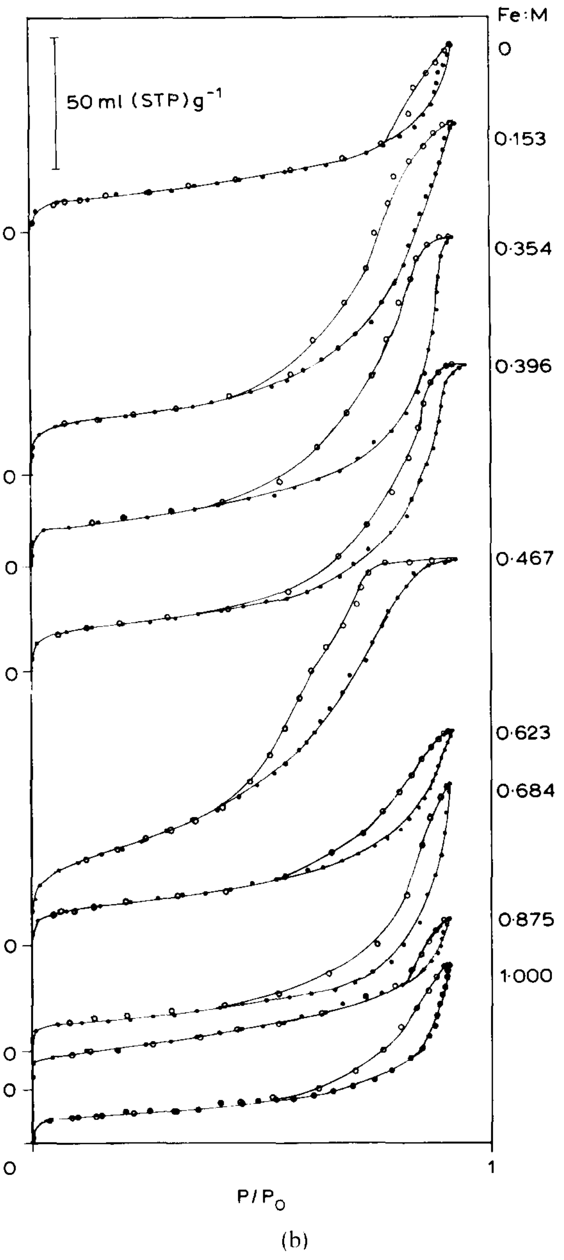
particle size for Co-containing samples. These particles consist of few lattice planes as shown by the reduced number of lattice fringes. The average particle size is *ca.* 15 nm, which is close to previously reported data for samples prepared by wet procedures.[3,4] The absence of lattice distortions in these ultrafine particles is also evident from the electron micrographs and may also be responsible for values of unit cell parameters close to those found in highly crystalline samples prepared by ceramic methods. These observations were checked by XRD line broadening analysis (Table 1). The size of the coherently diffracting domains normal to the 220 lattice planes (D_{220}) is in agreement with the electron micrographs and shows particles to consist of single domains. Additionally, microstrain contents ($\bar{e}_{220}$) are low except for those samples with Fe/(Fe + Co) between 0·35 and 0·47. The metastability of these samples will be discussed below—as these samples undergo a redistribution of cations at higher temperatures—and may be responsible for the higher level of lattice distortions. The above discussed characteristics of these samples (high dispersion and crystal perfection) can be considered to result from the homogeneous composition of the parent carbonates, which is preserved after the decomposition reactions.

On the other hand, the values of the unit cell parameter of cubic Mn-containing spinel phases (Table 1) are lower than those reported for Mn ferrites prepared by the thermal decomposition of oxalate precursors.[6] However, the O/M ratios shown in Table 1 are consistent with a higher cation-vacancy level in ex-carbonate samples, thus determining the smaller unit cell parameters. Additionally, the values of BET surface shown in Table 1 are larger than those reported in Ref. 6, thus indicating a higher dispersion of the samples obtained from carbonate precursors. The specific surface area of Mn-containing samples is in some cases lower than in Co/Fe spinels. However, the average particle size obtained from the high-resolution electron micrographs (Fig. 4) and line broadening analysis (Table 1) is also indicative of a high dispersion of mixed Mn/Fe spinels. However, the particles shown in Fig. 4 occur more frequently as aggregates, thus lowering the external surface by increasing the surface area of interparticle contacts.

A closer inspection of the N_2 adsorption isotherms in Fig. 3 reveals the occurrence of hysteresis phenomena, especially for Co-containing samples. This can be interpreted in terms of interparticle mesoporosity, on the basis of the application of the de Boer's *t* method of evaluation and by comparison



(a)



(b)

Fig. 3. N_2 adsorption–desorption isotherms at 77 K of decomposed Mn/Fe (a) and Fe/Co (b) carbonates.

with the electron micrographs of Fig. 4. The absence of intraparticle porosity, which is observed in the primary particles of Fig. 4, is of interest in the preparation of pelletized aggregates of these materials. However, the porous volume defined by the interparticle space should be minimized to obtain high-density ceramic bodies.

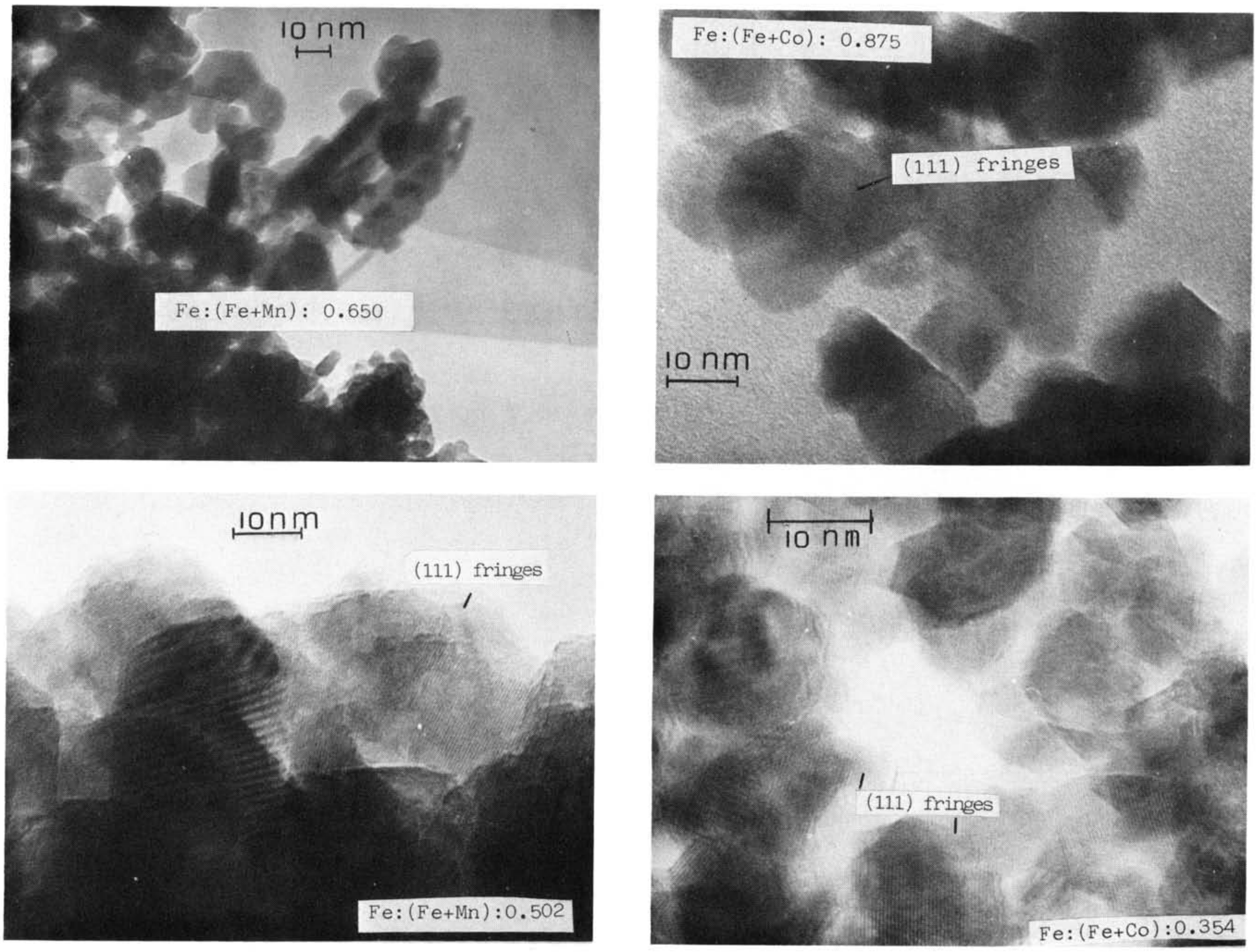
In order to obtain more information about the thermal behaviour of the spinel oxide samples, the isothermal treatment of the carbonate precursors was also carried out at 600°C. This treatment led to more complex products. Samples with Fe/(Fe + Co) ratios between 0·36 and 0·47 led to biphasic products with unit cell parameters ascribable to mixtures of Co_3O_4 and $CoFe_2O_4$ in proportions related to the initial Fe/(Fe + Co) ratios. The metastability of these samples was discussed above in the light of the microstrain contents. On the other hand, the high-temperature products of the thermal decomposition of Mn-containing carbonates were mixtures of phases structurally related to Mn_3O_4, α-Mn_2O_3 and α-Fe_2O_3, as shown by XDR. Nevertheless, the products with Fe/M close to 0·333 were pseudocubic tetragonal spinels that were used in the preparation of pelletized aggregates. Additional data on the samples prepared at 600°C revealed two complementary characteristics of ceramic interest: particle size increased to values higher than 30 nm and the average oxidation state of the metal ions decreased to values closer to those expected for stoichiometric M_3O_4 phases.

Following the above discussion, two ex-carbonate

Table 2. Chemical composition, crystallographic data and apparent density of sintered aggregates of selected samples

Chemical composition	*a* (*nm*)	*c*	d_x ($g\,cm^{-3}$)	d_α	$d_\alpha/d_x \times 100$
$Co_{0\cdot948}Fe_{2\cdot052}O_4$	$0{\cdot}8376_5$		5·299	5·089	96·04
$Mn_{2\cdot010}Fe_{0\cdot990}O_4$	$0{\cdot}5878_8$	$0{\cdot}8849_2$	4·988	4·741	95·05

d_x, X-ray density; d_α, apparent density.



(a) (b)

Fig. 4. Transmission electron micrographs of spinel oxides: (a) Mn/Fe system; (b) Fe/Co system.

oxide samples with selected Fe/M ratios were used to prepare pelletized aggregates at 1000°C of nominal composition $FeMn_2O_4$ and $CoFe_2O_4$. The apparent densities measured in these pellets are shown in Table 2. The theoretical densities were obtained from the X-ray diffraction data, that are in agreement with the JCPDS Diffraction files (10-319, 22-1086 and 24-734 files, respectively). From these measurements, a good densification of the ultrafine particles is observed, in accordance with previous work on ultrafine samples prepared by wet procedures.[4] Additionally, the scanning electron micrographs of the fractured surfaces of the pellets (Fig. 5) are in agreement with the density determination, as

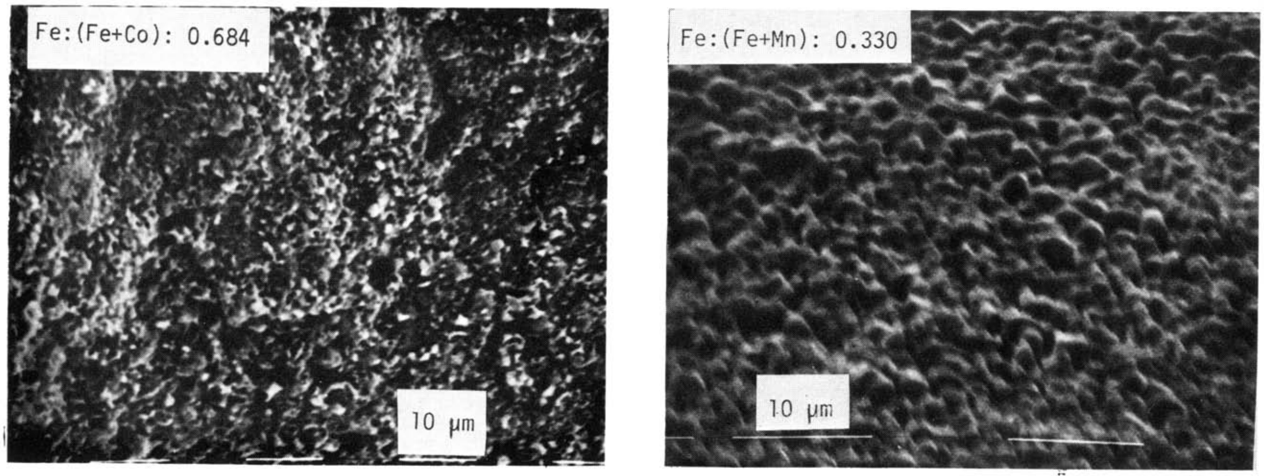


Fig. 5. Scanning electron micrographs of sintered samples.

little intergranular porosity is observed. At this point, it should be noted that the cation-reduction processes observed from 300 to 600°C in the ex-carbonate samples may induce the occurrence of pores to create ways of escape of the O_2 gas released in the reaction. However, this porosity was minimized by the pretreatment of the pelletized aggregates at 600°C for 1·5 h.

4 Conclusions

(1) Mixed oxides with spinel structures in the Mn–Fe–O and Fe–Co–O systems can be prepared in a wide compositional range by a simple procedure consisting in the low-temperature (300–400°C) thermal decomposition of mixed carbonate precursors.

(2) The powdered oxide products are cation-deficient oxides with a high homogeneity in composition and few lattice distortions. These materials are composed of aggregates of ultrafine particles with sizes close to 10 nm, that define a mesoporous system of variable magnitude. Some of these phases are metastable and suffer a cation redistribution at higher temperatures.

(3) Despite this metastability, selected compositions can be subjected to sintering processes that lead to spinel oxides with M_3O_4 stoichiometry at 1000°C, in agreement with the phase diagrams of the systems.[16,17] Pelletized aggregates of these compositions sinter at 1000°C to almost theoretical densities due to the presence of little interparticle porosity.

Acknowledgements

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