SYNTHESIS AND CHARACTERIZATION OF MANGANESE-COBALT SOLID SOLUTIONS PREPARED AT LOW TEMPERATURE

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ABSTRACT

Two extreme compositions of the manganese-cobalt oxide system $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ namely Co_3O_4 ($x = 0$) and MnCo_2O_4 ($x = 1$) were prepared in powder form at low temperature by thermal decomposition of nitrates in air. The synthesis was conducted at 150°C. The oxides obtained were characterized by different techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), surface area determination using the Brunauer-Emmett-Teller (BET) method, thermogravimetric analyses (TGA) and oxidation power (OP). XRD analysis reveals that the oxides crystallize in a cubic spinel-type structure with a unit cell parameter (a_0) that increases as cobalt is replaced by manganese. The MnCo_2O_4 showed 70 m^2g^{-1} and 13 nm of specific surface area and crystallite size respectively. The crystallite was bigger (20nm) when cobalt-manganese oxide is prepared as a thin film. Both compounds exhibited nanometric size. The cationic distributions proposed for both oxides on the basis of the physicochemical characterization results showed an excellent agreement with those obtained from the XRD data refinement performed using the Rietveld method.

Keywords: Manganese cobalt oxide, Mixed oxides, Spinel, Solid Solution, Manganese-cobalt distribution

INTRODUCTION

Spinel type oxides from transition metals, particularly the manganese-cobalt oxide family, are interesting systems because of their potential for a variety of applications in the conversion of energy^{1,2}. Many different synthetic routes have been attempted to prepare $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ oxides in powder form³. The commonest method for the preparation of these spinels has been the thermal decomposition of nitrate precursors at different temperatures. From a practical point of view, the search is oriented to obtain the highest specific area in addition to the highest intrinsic activity. Mixed valence oxides have rather low specific surface areas, mainly when they are prepared at high temperature by conventional ceramic methods or decomposition of dry salts routes. However, they may reach higher specific surface areas when they are obtained at lower temperatures by thermal decomposition of suitable precursors⁴.

In the thermal process of powder preparation, the higher specific areas are obtained at lower temperatures⁵. On the other hand, when the powders are synthesized at low temperatures from aqueous solutions, water molecules and OH groups end up attached to the oxide structure⁴. Besides, thermally formed oxides are as a rule non-stoichiometric. A common feature is that non-stoichiometry decreases when the calcination temperature increases, thus paralleling the decrease in surface area⁶. The solid-state properties of the two extreme compositions of a series of mixed oxides $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ ($0 \leq x \leq 1$), i.e. the spinel oxides of cobalt Co_3O_4 ($x = 0$) and of manganese and cobalt MnCo_2O_4 ($x = 1$), have been more intensively investigated than the intermediate compositions (with x varying from $x = 0$ to $x = 1$ and with $\Delta x = 0.25$).

The formula of a binary spinel oxide is $\text{A}[\text{B}_2]\text{O}_4$ in which A is a cation tetrahedrally coordinated with the oxygen while the B cation is octahedrally coordinated with the oxygen. Each cubic unit cell contains 8 formal units $\text{A}[\text{B}_2]\text{O}_4$, that is to say it corresponds to $\text{A}_8\text{B}_{16}\text{O}_{32}$. Spinel is usually classified as normal, inverted or random⁷.

Owing to the multiple oxidation states that the mixed oxides formed in the Mn-Co-O system can adopt, the determination of the oxidation states and cation distributions among both the tetrahedral and octahedral sublattices of the spinel structure are not simple tasks⁷⁻⁹. There is overwhelming evidence in the literature that the distribution of the cationic oxidation states among the different crystallographic sites greatly depends on the preparation conditions and also determines the textural and morphological characteristics of the powder oxides¹⁰.

Early investigations by Wickham and Croft¹¹ and Naka et al.¹² have shown that a single stable phase of the cubic manganese-cobalt spinel exists at 1000°C only for the $0 \leq x \leq 1.3$ composition range. It is now widely accepted in the literature¹³⁻¹⁹ that Co_3O_4 exhibits a normal cationic

distribution, with low spin Co^{3+} in octahedral sites and high spin Co^{2+} in tetrahedral sites: $\text{Co}^{2+}[\text{Co}^{\text{III}}\text{Co}^{\text{III}}]\text{O}_4$. In contrast, the cationic distribution of MnCo_2O_4 is not well established. Several cationic distributions have been proposed in stoichiometric MnCo_2O_4 and non-stoichiometric $\text{Mn}_x\text{Co}_{3-x}\text{O}_{4+d}$ oxides on the basis of (i) electrical conductivity¹⁰: $\text{Co}^{2+}[\text{Co}^{2+}\text{Mn}^{4+}]\text{O}_4$ or $\text{Co}^{3+}[\text{Co}^{3+}\text{Mn}^{2+}]\text{O}_4$, ii) magnetism: $\text{Co}^{2+}[\text{Co}^{3+}\text{Mn}^{3+}]\text{O}_4$ by Wickham and Croft¹¹ and $\text{Co}^{2+}[\text{Co}^{2+}\text{Mn}^{4+}]\text{O}_4$ by Blasse²⁰, and iii) neutron diffraction and magnetism measurements: $\text{Co}^{2+}[\text{Co}^{3+}\text{Mn}^{3+}]\text{O}_4$ by Boucher et al.²¹. $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ oxides are commonly described as being inverse spinels in which the manganese cations show preference for octahedral sites. Studies of the surface composition of MnCo_2O_4 by XPS have shown that the Co is present as Co^{2+} and Co^{3+} while Mn is mainly present as Mn^{3+} ions²². Ravindranathan et al.²³ reported on the synthesis of MnCo_2O_4 from its organic precursor decomposition below 250°C. Yamamoto et al.²⁴ used neutron diffraction technique to study the oxide MnCo_2O_4 synthesised by a wet procedure at 80°C, and have proposed $\text{Mn}_{1-x}\text{Co}_x[\text{Mn}_x\text{Co}_{2-x}]\text{O}_4$ as the atomic distribution, where x is the inversion parameter. On the basis of chemical analysis, DRX, TGA, DTA and oxidation power measurements, Gautier, Fuentealba and Cabezas²⁵ proposed a global formulae and ionic stoichiometry of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ ($1 \geq x \geq 0.25$) prepared at 400°C.

Depending on the preparation method and the calcination temperature, Gautier et al. have suggested the cationic distributions: $\text{Co}^{2+}[\text{Co}^{3+}\text{Mn}_{0.35}^{2+}\text{Mn}_{0.29}^{3+}\text{Mn}_{0.36}^{4+}]\text{O}_4$ ²⁶ and $\text{Co}^{2+}[\text{Co}_{0.95}^{3+}\text{Mn}_{0.015}^{2+}\text{Mn}_{0.50}^{3+}]\text{O}_4$ ²⁷. The occurrence of Mn^{4+} cations in octahedral sites has been again considered by Jabry, Rousset and Lagrange²⁸ from X-ray and electrical conductivity measurements: $\text{Co}^{2+}[\text{Co}_x^{2+}\text{Co}_{2(1-x)}^{3+}\text{Mn}_x^{4+}]\text{O}_4$. Rios et al.¹ have prepared by thermal decomposition at 400°C of nitrates salts the entire series $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ ($0 \leq x \leq 1$) and proposed the corresponding cationic distributions. In the recent past we have undertaken the study of the title compound by spray pyrolysis at 150°C of the two extreme compositions Co_3O_4 and MnCo_2O_4 , but were unable to obtain cationic distribution measurements due to material paucity⁵. Co_3O_4 was prepared by a sol-gel process at 300°C²⁹ with large

specific area ($27 \text{ m}^2 \text{ g}^{-1}$) while De Vidales et al.⁴ have prepared MnCo_2O_4 by a sol-gel route at 80°C with larger specific surface area. The temperature at which the Co_3O_4 spinel oxide is formed changes with the heating rate. Pope et al.³⁰ observed that the decomposition was already completed at 200°C , when the heating rate was lowered, while Garavaglia et al.³¹ reported that at sufficiently long times Co_3O_4 is formed at 150°C (24 h).

In this work, we report the successful preparation at low temperature, on the two extreme compositions of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ material, Co_3O_4 ($x = 0$) and MnCo_2O_4 ($x = 1$), using a thermal decomposition procedure with proper salt precursors. A series of physicochemical measurements have enabled us to propose the cationic distributions which have been confirmed by the application of the Rietveld structural analysis method. A further crystallographic study for the rest of the oxides family, namely for $x = 0.25, 0.5$ and 0.75 , and a study of the effects of solid state properties of the entire series of the spinel-type $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ ($0 \leq x \leq 1$) compounds on their electrocatalytic properties, are currently in progress.

EXPERIMENTAL

Preparation of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ oxides

The chemical synthesis of the polycrystalline compounds $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ ($x = 0$ and 1.0) were conducted by thermal decomposition of nitrate solutions.

Co_3O_4 synthesis

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka p.a. ref. 60833) was allowed to dissolve in its crystallization water by gradually heating it up to 100°C . The solution was then evaporated and the residual solid nitrate was further decomposed in air at 150°C .

MnCo_2O_4 synthesis

The aqueous precursor solutions were made up of cobalt and manganese nitrate salts (analytical grade) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka p.a. ref. 60833) and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck p.a. ref. 5942), whose concentrations were 0.100 and 0.0947 M , respectively. To avoid metal hydroxide precipitation, these solutions were slightly acidified with 1 mL of concentrated HNO_3 (Merck p.a.) per liter. The expected stoichiometry was obtained by mixing the required amounts of the starting solutions to yield the desired concentration. The overall concentration of the mixed solutions was 0.08 M .

The above mentioned cobalt nitrate and the corresponding mixture were separately heated slowly on a sand bath to evaporate the water until a dry solid residue was obtained. Further decomposition in air at 150°C was conducted until complete cessation of the red-coloured nitrous vapours (NO_x), coming from the nitrates decomposition. The residual powder was carefully ground, sieved (400 mesh) and then calcined inside a tubular furnace for 24 hours in an alumina crucible at 150°C in air. After cooling to room temperature (RT), the resulting powder was again submitted to prolonged cycles of grinding and reheated at the same temperature, to ensure the total decomposition of the oxides. Total calcination time was 5 days. All the final products were black in colour. Once the binary oxides formation was accomplished the samples were stored in a desiccator under vacuum.

Chemical analysis

The accurate cationic concentrations of Co and Mn both in the mother liquors and in the final products were controlled by Induced Coupled Plasma-Optical Emission (ICP-OE) Spectroscopy, using an Optima 2000 DV Perkin-Elmer apparatus, not only for checking their actual rate, but also because there is always some doubt about the composition of manganese nitrate due to the hygroscopic character of the starting salt. For these classical analyses, the samples were dissolved in acidic media and then the metallic cation ratios were determined using Mn and Co standards from Perkin-Elmer (1 mg mL^{-1}). The cationic Co/Mn ratios present in solution were satisfactorily retained in the oxide powders. Within experimental error ($\pm 2\%$), the composition of all the compounds were in good agreement with the expected ones.

X-ray diffraction

Crystallographic structure and purity of the samples were carried out by X-ray powder diffraction (XRD), using a Siemens D500 diffractometer at RT employing a Cu anode $\text{K}\alpha_1$ ($\lambda = 0.154060 \text{ nm}$) and $\text{K}\alpha_2$ ($\lambda = 0.1540431 \text{ nm}$) in Bragg-Brentano geometry. The voltage and intensity current were set to 40 kV and 30 mA , respectively. The data were collected in steps of 0.02° (2θ) with a fixed-time counting of 5 s . Profiles were measured in the range 10° to 110° (2θ) since no detectable peaks were observed beyond these values. The refinement of X-ray diffraction results was performed using the Rietveld's profile analysis method with the Fullprof Suite program³².

SEM analysis

In order to estimate the average aggregate size and crystallinity degree of the oxides, the microstructures of the powders were examined by scanning

electron microscopy (SEM) using a JEOL apparatus (JSM 5410). The details of surface morphology were studied at magnifications of up to $5000\times$ by scanning electron microscopy.

Thermogravimetric analysis

The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves were obtained using a TA Instruments SDT 2960 under a dry static air atmosphere. About a 40 mg sample was used in each run, and $\alpha\text{-Al}_2\text{O}_3$ was the inert reference material. The material was heated from RT up to 800°C at a constant rate of $20^\circ\text{C min}^{-1}$.

Specific surface areas

The specific surface areas of the oxides were measured by the Brunauer-Emmett and Teller (BET) method. Nitrogen physisorption measurements of the fresh samples were performed in a standard Sorptometer Micromeritics ASAP 2010.

Oxidation power $q(x)$.

The oxidation power $q(x)$ of the oxide can be defined as the degree of oxidation power of the spinel with regard to a soft reduction agent³³. This parameter (eq mol^{-1}) was determined by chemical reduction of the oxide cations M^{n+} with $n \geq 3$ until oxidation state 2 was reached using a mild reducing agent, such as vanadyl sulphate sulphuric solution (1 N VOSO_4) according to the reaction:

This measurement reflects the quantity of electrons per mole of $(\text{Mn}_x\text{Co}_{3-x})^{8+}$ with $q(x) > 2$ necessary to level all oxidation states to 2. The oxide samples (50 mg approximately) were dissolved in a known excess amount (50 mL) of VOSO_4 (Merck p.a.) in sulfuric acid solution (to avoid cationic hydrolysis). Because of the extended periods of digestion required to dissolve the samples, the mixture was heated at 90°C for 48 hours. After complete dissolution of the oxide, the unreacted VOSO_4 was potentiometrically titrated with 1 N KMnO_4 solution, which had been previously standardized with oxalate solution according to McBride's method³⁴. The oxidation power was calculated according to the equation:

$$q(x) = (V_{\text{VO}} N_{\text{VO}} - V_{\text{K}} N_{\text{K}}) M_{\text{ox}} / m_{\text{ox}} \quad (1)$$

where V_{VO} and N_{VO} and V_{K} and N_{K} are the volume and concentration of the VOSO_4 solution and the KMnO_4 solution, respectively, M_{ox} and m_{ox} corresponding to the molar mass and weight of the oxide. Each determination was made at least three times. The overall standard deviation was ± 0.02 .

A cationic distribution derived from the X-ray diffraction pattern and the oxidation power were computed using the method of Poix³⁵ based on the best fit with the equation: $a = 2.0995a + [5.18182b^2 - 1.4107a^2]^{1/2}$ in which $\alpha = \sum x_i (M_i - O)_{\text{Td}} / \hat{\alpha} x_i$ and $\beta = \hat{\alpha} x_i (M_i - O)_{\text{Oh}} / \hat{\alpha} x_i$, with x_i being the stoichiometric coefficient of the cation M_i and $M_i - O$ the cation oxygen distances in the tetrahedral (Td) and octahedral (Oh) sites according to the Shannon and Prewitt data³⁶ and, considering the energetic preference of a cation for either site, according to Paul and Basu³⁷. The presence of the Mn^{3+} and Mn^{4+} ions in octahedral sites and the occupancy of tetrahedral sites by the Co^{2+} and Mn^{2+} ions for the cobalt-manganese spinel have been already established in the literature³⁸⁻⁴⁰.

RESULTS AND DISCUSSION

3.1. Structural properties of Co_3O_4 and MnCo_2O_4 oxides.

Figure 1A. Rietveld refinement plots for Co_3O_4 . The experimental and calculated intensity data are plotted as dotted and solid lines respectively and the difference ($I_{\text{exp}} - I_{\text{cal}}$) below.

Figure 1B. Rietveld refinement plots for MnCo_2O_4 . The experimental and calculated intensity data are plotted as dotted and solid lines respectively and the difference ($I_{\text{exp}} - I_{\text{cal}}$) below.

Figures 1A and 1B show the X-ray diffraction patterns of the Co_3O_4 and MnCo_2O_4 phases respectively. Even if the crystalline state is not better defined due to the low temperature of synthesis⁴¹, Rietveld analysis shows single phases corresponding to the expected compounds which crystallize in the face centered cubic system spinel type, spatial group o^7 (Fd3m). All the main peaks (indicated by their hkl indices) could be indexed by comparison with the diffraction patterns of Co_3O_4 and MnCo_2O_4 . Both the position and the relative intensities of the diffraction lines were found to be in good agreement with the ASTM X-ray powder data files JCPDS-ICDD for Co_3O_4 and MnCo_2O_4 , thus showing that a single phase of each component was present. A remarkable common feature of the X-ray spectra of both spinel oxides prepared at such a low temperature was the good definition of the diffraction lines. The mayor peak in both XRD profiles was found to correspond to the (311) crystallographic plane. The Co_3O_4 lattice constant ($a_0 = 0.8079$ nm) shows an acceptable good agreement with the 8-418 ASTM file value of 0.8084 nm for a product prepared at 850 °C. For MnCo_2O_4 a more pronounced discrepancy was observed ($a_0 = 0.8089$ nm) with the 23-1237 ASTM file value of 0.8269 nm, not only due to differences between the preparation method (ceramic procedure), but also due to the temperature of the preparation (720°C). This higher variation for MnCo_2O_4 suggests the presence of cations with a high oxidation state that must be distributed in a smaller size cell and a cationic stoichiometric deficiency should not be ruled out.

The diffractograms in Fig. 1 show a loss of crystallinity going from Co_3O_4 to MnCo_2O_4 . Broader diffraction peaks at the same positions were observed indicating that MnCo_2O_4 (13 nm) have a smaller crystallite size than Co_3O_4 (45nm) (see Table I).

Table I. Structural and refinement parameters of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ ($x = 0$ and 1).

Compound	Lattice parameter $a_0 \pm 0.0003$ / nm	R_{Bragg}	GOF	Average crystallite size /nm
Co_3O_4	0.8078 ₈	2.056	1.143	45
MnCo_2O_4	0.8089 ₄	2.161	1.241	13

The fractional coordinates of the atoms in the cell as well as the starting refinement were established on the basis of the model by Knop et al.¹⁸ for Co_3O_4 ($a_0 = 0.80835$ nm), which provides the best results for the fit. With this model the families of planes shown in Fig. 1 were indexed. The results of applying the structure refinement procedure to the experimentally determined intensities for the entire set of diffraction lines are shown in table I. This table includes the lattice parameter, the Bragg factor and the goodness of fit (GOF) that provides the refinement. Besides, it also shows the coherent diffraction size (crystallite) and the non-uniform micro deformation values obtained using the Wilson equation⁴² and full width at half maximum (FWHM) in the case of pseudo Voigt function of the peaks that are shown. The cubic cell parameter increases with an increase in manganese content, as expected. This result was interpreted as an effect of the substitution of Co-cations by larger Mn-cations⁴³ as can be seen in Table II. The decrease of the lattice parameter of the Co_3O_4 with respect to the starting model can be attributed to the low temperature of the preparation.

Table II. Effective ionic radii. hs = high spin, ls = low spin.

Ion	Coordination	Spin State	Ionic Radius / nm	Ion	Coordination	Spin State	Ionic Radius / nm
Co^{2+}	IV	hs	0.058	Mn^{2+}	IV	hs	0.066
	VI	ls	0.065		VI	ls	0.067
		hs	0.0745			hs	0.083
Co^{3+}	VI	ls	0.0545	Mn^{3+}	VI	ls	0.058
		hs	0.061			hs	0.0645
				Mn^{4+}	IV		0.039

The powders of the oxides present an average crystal size in the range of 13-45 nm, confirming that the oxide particles were actually nanometric. The low crystal size can be explained by the low temperature used in the preparation of the oxides.

SEM

Figures 2A and 2B show SEM micrographs of the samples Co_3O_4 and MnCo_2O_4 . The magnified images show differences in the morphology between the products. From a morphological point of view the particles of Co_3O_4 are agglomerated while MnCo_2O_4 shows particles geometrically defined (nearly trapezoidal crystallites). The average grain size of both samples measured from SEM micrographs lies in the range 1 – 8 nm.

Figure 2A. SEM micrographs of the Co_3O_4 powder. X = 5000.

Figure 2B. SEM micrographs of the MnCo_2O_4 powder. $X = 5000$.

Thermogravimetric studies

The thermogravimetric analysis (TGA) in air of dried Co_3O_4 and MnCo_2O_4 powders are presented in Figure 3 and 4 respectively. Both TG curves show a thermal decomposition process involving several steps that begin at RT and finish near 600°C . On the curves, mainly three regions of mass loss can be distinguished. The processes occurring during the course of heating should include: physisorbed water evolution, water from OH groups adsorbed onto the surface of the oxide particles⁴⁴ and a progressive loss of the excess oxygen in the non-stoichiometric oxide³¹, namely $\text{Co}_3\text{O}_{4+d}$ and $\text{MnCo}_2\text{O}_{4+d}$. Gyrdasova et al.⁴⁵ have prepared MnCo_2O_4 from manganese cobalt oxalate. They reported the formation of a cubic spinel phase at 200°C . According to TG data the difference between the calculated and experimentally determined values of mass loss points to a higher oxygen content and consequently cationic deficiency. Further heating of MnCo_2O_4 at 700°C make lose oxygen and converts to the stoichiometric spinel MnCo_2O_4 . At this temperature its lattice parameter is $a_o = 0.8226$ nm. The increase in a_o is likely due to the reduction of manganese or cobalt.

Figure 3. TGA curves recorded on Co_3O_4 . $v = 20^\circ\text{C min}^{-1}$, air atmosphere.

Figure 4. TGA curves recorded on MnCo_2O_4 . $v = 20^\circ\text{C min}^{-1}$, air atmosphere.

Specific surface areas

The BET analysis performed on MnCo_2O_4 gave an average specific surface area of $70 \text{ m}^2 \text{ g}^{-1}$. This value is higher than the one reported in the literature for MnCo_2O_4 prepared by a sol-gel process at 80°C with a surface area of $34 \text{ m}^2 \text{ g}^{-1}$; the area increased to $44 \text{ m}^2 \text{ g}^{-1}$ when annealing at 200°C ⁴.

Oxidation power

The amount of equivalent per oxide mole, $q(x)$, is higher for MnCo_2O_4 . This suggests that the replacement of Co ions by Mn ions at the B octahedral sites would generate Mn ions with higher oxidation states.

Cationic distributions

A major challenge associated to the Mn-Co-O spinel-type systems is the determination of the metal oxidation states and cation distributions among the tetrahedral (labelled as A sites) and octahedral (B sites) sublattices of the spinel-related structure⁴⁶. To put forward a tentative cation distribution for the compounds, the method of characteristic distances (invariants) developed by Poix³⁵ has been used along with literature data. In Mn-Co spinels the most likely cationic distributions reported in the literature indicates predominantly the presence of Co^{2+} and Mn^{2+} ions at A sites and Co^{3+} , Mn^{3+} and Mn^{4+} ions at B sites leading to an ionic configuration⁴⁷. Table III gathers the experimental values of the lattice constant, a_o , and the global oxidizing power, $q(x)$, from which best fitted cationic distributions displayed in Table IV were established. The values for the calculated parameters a_o and $q(x)$ on the basis of these cationic distributions are also shown in Table III.

Table III. Experimental and calculated values of the lattice constant a_o and global oxidizing power $q(x)$ of the oxides Co_3O_4 and MnCo_2O_4 .

Compound	a_o / nm		$q / \text{eq. mol}^{-1}$	
	$a_o \text{ exp}$	$a_o \text{ calc}$	q_{exp}	q_{calc}
Co_3O_4	0.80788	0.80793	1.92	1.94
MnCo_2O_4	0.80894	0.80896	2.50	2.48

Table IV. Cationic distributions for the oxides Co_3O_4 and MnCo_2O_4 .

Compound	Cationic distributions	R_{Bragg}	GOF
Co_3O_4	$\text{Co}^{2+}_{0.85} \text{Co}^{3+}_{0.15} [\text{Co}^{3+}_{1.79} \text{Co}^{2+}_{0.18} \square_{0.03}]$	2.056	1.143
MnCo_2O_4	$\text{Co}^{2+}_{0.88} \text{Mn}^{2+}_{0.12} [\text{Co}^{3+}_{0.87} \text{Co}^{2+}_{0.22} \text{Mn}^{3+}_{0.09} \text{Mn}^{4+}_{0.76} \square_{0.06}]$	2.161	1.241

We are now able to propose the most probable cationic distribution of the compounds as a result of a coherent study that includes:

- Co^{n+} -O and Mn^{n+} -O distances, where n can be 2, 3 or 4³⁵, considering cation lattice site preferences.
- similarities between the calculated global oxidizing power q_{calc} values and the experimental ones q_{exp} .
- the excellent fit between XDR results and the results obtained from the Rietveld refinement.

CONCLUSIONS

In earlier work ¹⁰, the preparation of the title compounds by spray pyrolysis at the same temperature (150°C) as film electrodes was successfully undertaken by us, under rigorous preparation conditions with $a_o = 0.8068$ and $q(x) = 1.6$ for Co_3O_4 , and $a_o = 0.8197$ and $q(x) = 1.9$ for MnCo_2O_4 . Following the present results on the studied oxides we have now successfully accomplished the preparation of low temperature Co_3O_4 and MnCo_2O_4 materials by thermal decomposition of nitrate precursors. The syntheses of the compounds require a thermal treatment for several days to achieve thermal equilibrium. The formation of a cubic spinel-type phase for Co_3O_4 and MnCo_2O_4 has been achieved. The spinel oxides thus prepared have a large specific surface area ($70 \text{ m}^2 \text{ g}^{-1}$) and both types are nanometric materials. The cobalt oxide showed 45 nm of crystallite size while manganese-cobalt oxide only 13 nm. However when MnCo_2O_4 was prepared as a thin film using the spray pyrolysis technique at the same temperature, the crystallite was bigger ⁵ (20 nm) thus showing the effect of the preparation method.

The cationic distribution proposed on the basis of a series of physicochemical measurements show an excellent agreement with the cationic distribution obtained from the Rietveld structural analysis method of XRD data.

The preparation and the crystallographic study of the rest of the oxides family ($x=0.25$ and 0.75) is currently in progress. A further electrochemical characterization study will complete this work.

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