

Thermal Behavior in Air and Reactivity in Acid Medium of Cobalt Manganese Spinel $Mn_xCo_{3-x}O_4$ ($1 \leq x \leq 3$) Synthesized at Low Temperature

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The thermal behavior in air of manganese cobalt oxides $Mn_xCo_{3-x}O_4$ ($1 \leq x \leq 3$) obtained at low temperature has been studied by X-ray powder diffraction using the Rietveld method of structural refinement. The existence of three well-defined solid solutions is established, and their field of existence delimited. Cubic $Fd3m$ spinel-type solid solution is formed in the compositional range $x \leq 1.4$, the cell parameter ranging from 8.0769(2) for Co_3O_4 ($x = 0$) to 8.3216(3) Å ($x = 1.4$). The same trend is observed for the cell constants a and c of the tetragonal (space group $I4_1/amd$) single phase formed in the interval $2.0 \leq x \leq 3.0$, with distortion parameter (c/a' , $a' = a\sqrt{2}$) ranging from 1.139 to 1.162. For samples $1.4 < x < 2.0$ quenched from 1000 °C, the formation of a tetragonal single phase has been attained for the first time. For this solid solution, the distortion parameter varies from 1.04 to 1.135. Soaking of spinel-like oxides with 0.25 M HCl for 24 h at room temperature yields cubic cobalt deficient spinels, through a topotactic reaction. A redox mechanism that accounts for this transformation is pointed out. For the oxide $Mn_xCo_{3-x}O_4$ ($x = 2.6$), the acid treatment leads to the formation of a λ - MnO_2 type phase ($a = 8.033(2)$ Å) with a very low cobalt content ($\approx 3.2\%$).

Introduction

It is well-known that morphological and textural parameters play such an important role that, in some cases, take control and determine the physicochemical properties of materials. In this connection the preparation of many transition-metal oxides with cubic or tetragonal spinel-type structure has been attempted in the past by using many different synthesis procedures. They can lead to the obtention of these oxides with well-defined properties, i.e., homogeneous compositions, small particle size, high reactivity, etc. Among them, the use of inorganic¹⁻⁵ and organic precursors⁶⁻¹⁰ showing low decomposition temperatures, as well as the so-called "wet methods" based on the coprecipitation of the involved cations,¹¹⁻¹³ constitute successful alternatives to the traditional ceramic procedure. Spinel-type oxides

formed in the Co-Mn-O system have been formerly synthesized by the ceramic method,¹⁴⁻¹⁶ they have also been prepared at moderate temperature (400 °C) from mixed carbonates¹⁷ or, more recently, at low temperature (80-200 °C) by coprecipitation with butylamine of mixed Co^{2+}/Mn^{2+} chloride solutions.^{18,19} The solids $Mn_xCo_{3-x}O_4$ ($0 \leq x \leq 3$) obtained at 1000 °C under different atmospheres have been investigated by Naka et al.¹⁶ In air, a cubic spinel single phase was found in the compositional range $0 \leq x \leq 1.3$; from $x = 1.9$ to 3.0 a tetragonal spinel was identified. However, for $1.3 < x < 1.9$ a mixture of cubic and tetragonal spinels was reported to be formed.

Spinel-type manganese oxides are widely used as precursors in the preparation of λ - MnO_2 ($[\square]_A[Mn_2]_BO_4$). This oxide is of technological interest due to its applications as cathode material for rechargeable cells.^{20,21} Many different approaches are currently being followed

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- (1) Vidyasagar, K.; Gopalakrishnan, J.; Rao, C. N. R. *Inorg. Chem.* **1984**, *23*, 1206.
- (2) Angelov, S.; Zhecheva, E.; Petrov, K.; Menandjiev, D. *Mater. Res. Bull.* **1982**, *16*, 235.
- (3) Petrov, K.; Markov, L. J. *Mater. Sci. Lett.* **1985**, *4*, 711.
- (4) Klissurski, D. G.; Uzunova, E. L. *Chem. Mater.* **1991**, *3*, 1060.
- (5) Wright, P. A.; Natarajan, S.; Thomas, J. M.; Gai-Boyes, P. L. *Chem. Mater.* **1992**, *4*, 1053.
- (6) Rousset, A.; Chassagneux, F.; Paris, J. *J. Mater. Sci.* **1986**, *21*, 3111.
- (7) Guillot, B.; Guendouzi, M. el; Rousset, A.; Tailhades, P. *J. Mater. Sci.* **1986**, *21*, 2626.
- (8) Peshev, P.; Toshev, A.; Gyurov, G. *Mater. Res. Bull.* **1989**, *24*, 33.
- (9) Ravindranathan, P.; Mahesh, G. V.; Patil, K. C. *J. Solid State Chem.* **1987**, *66*, 20.
- (10) Tsumura, T.; Shimizu, A.; Inagaki, M. *J. Mater. Chem.* **1993**, *3*, 995.
- (11) Yamamoto, N.; Higashi, S.; Kawano, S.; Achiwa, N. *J. Mater. Sci. Lett.* **1983**, *2*, 525.

- (12) Yamamoto, N.; Kawano, S.; Achiwa, N.; Higashi, S. *J. Jpn. Soc. Powder Metal.* **1983**, *30*, 48.
- (13) Pathak, A.; Mukhopadhyay, D. K.; Pramanik, P. *Mater. Res. Bull.* **1992**, *27*, 155.
- (14) Buhl, R. *J. Phys. Chem. Solids* **1969**, *30*, 805.
- (15) Boucher, B.; Buhl, R.; di Bella, R.; Perrin, M. *J. Phys. (Paris)* **1970**, *31*, 113.
- (16) Naka, S.; Inagaki, M.; Tanaka, T. *J. Mater. Sci.* **1972**, *7*, 441.
- (17) Jiménez-Mateo, J. M.; Morales, J.; Tirado, J. L. *J. Solid State Chem.* **1989**, *82*, 87.
- (18) Martín de Vidales, J. L.; García-Martínez, O.; Vila, E.; Rojas, R. M.; Torralvo, M. *J. Mater. Res. Bull.* **1993**, *28*, 1135.
- (19) Rojas, R. M.; Vila, E.; García-Martínez, O.; Martín de Vidales, J. L. *J. Mater. Chem.* **1994**, *4*, 1635.
- (20) Tackeray, M. M.; de Kock, A.; Rossouw, M. H.; Liles, D. C.; Bittihn, R.; Hoge, D. *J. Electrochem. Soc.* **1992**, *139*, 363.
- (21) Tarascon, J. M.; Wang, E.; Shokoohi, F. K.; McKinnon, W. R.; Colson, S. *J. Electrochem. Soc.* **1991**, *138*, 2859.

Table 1. Phases Identified and Distortion Parameter c/a' for $Mn_xCo_{3-x}O_4$, $x = 1.4, 1.6, 2.0, 2.6,$ and 3.0 , between 200 and 1000 °C^a

T (°C)	x							
	1.4	1.6	2.0	c/a'	2.6	c/a'	3.0	c/a'
200	C	T + R	T	1.125	T	1.154	T	1.161
300	C	T + R	T	1.131	T	1.150	T	1.160
400	C	T	T	1.138	T	1.152	T + B(39%)	1.160
500	C	T + C	T	1.140	T + B(8%)	1.153	T + B(99%)	1.163
600	C	T + C	T	1.143	T + B(88%)	1.148	B	
700	C	T + C	T	1.145	T + B(88%)	1.148	B	
800	C	T + C	T	1.146	T + B(82%)	1.152	B	
900	C	T + C	T	1.144	T	1.155	B	
1000	C	T + C	T	1.139	T	1.155	T + B(9%)	1.162

^a C = cubic spinel, T = tetragonal spinel, R = $Co_8O_6Cl_4 \cdot 7H_2O$, B = bixbyite α - Mn_2O_3 , $a' = a\sqrt{2}$.

in an attempt to successfully prepare this phase, among them topotactic extraction of Li^+ from lithium-containing manganese spinel oxides^{22-24,36} or of Mg^{2+} from magnesium manganese spinel oxides.^{25,26} However, to the best of our knowledge, extraction of Co^{2+} from cobalt manganese spinels has never been reported.

In a previous paper we have studied the thermal behavior under different atmospheres of the cubic spinel-type oxides $Mn_xCo_{3-x}O_4$ ($0 \leq x \leq 1.0$) obtained through the procedure there described.¹⁹ In this paper we report on the evolution with temperature of spinel-like materials $Mn_xCo_{3-x}O_4$ ($1 \leq x \leq 3$) obtained by the low-temperature synthesis route also applied to the preparation of some other metal oxides.^{18,27,28} For materials $1.4 < x < 2.0$, the formation of a tetragonal single phase with distortion parameter c/a' ($a' = a\sqrt{2}$) is reported for the first time. When spinels $Mn_xCo_{3-x}O_4$ heated at 200 °C are treated with a HCl solution, cobalt is partially removed from the A sites. In the range ($1 \leq x \leq 3$) here considered and for $x \leq 2.6$, cubic cation deficient spinel-type oxides are obtained. Particularly, for $x = 2.6$ the formation of a λ - MnO_2 type phase, with a cobalt content of $\approx 3.2\%$ is achieved.

Experimental Section

A series of mixed oxides $Mn_xCo_{3-x}O_4$ with x varying from $x = 1$ to $x = 3$ in steps of $\Delta x = 0.2$ have been synthesized. Mixed Co^{2+} and Mn^{2+} solutions were prepared by dissolving stoichiometric amounts of the corresponding metal chlorides in distilled water. The cations were coprecipitated by slow addition (1 mL min^{-1}) of n -butylamine (1 mol L^{-1}), up to pH ≈ 10.5 . A detailed description of the synthesis procedure has been published elsewhere.^{19,27} Some particular compositions ($x = 1.4, 1.6, 2.0, 2.6,$ and 3.0) were systematically and cumulatively heated in air between 200 and 1000 °C in steps of 100 °C, kept at each defined temperature for 5 h, and then allowed to slow cool within the furnace (see Table 1). On the other hand, samples $Mn_xCo_{3-x}O_4$ ($1.4 \leq x \leq 2$) were also heated at 1000 °C for 3 h and then quenched to room temperature. Samples (1 g) of $Mn_xCo_{3-x}O_4$ ($1 \leq x \leq 3$) heated at 200 °C were reacted with 200 mL of a 0.25 M ($1 \text{ M} = 1 \text{ mol L}^{-1}$) HCl for 24 h at room temperature with continuous and vigorous stirring.

(22) Hunter, J. C. *J. Solid State Chem.* **1981**, *39*, 142.

(23) Feng, Q.; Miyai, Y.; Kanoh, H.; Ooi, K. *Langmuir* **1992**, *8*, 1861.

(24) Liu, Y. F.; Feng, Q.; Ooi, K. *J. Colloid Interface Sci.* **1994**, *163*, 130.

(25) Miyai, Y.; Ooi, K.; Katoh, S. *Sep. Sci. Technol.* **1988**, *23*, 179.

(26) Miyai, Y.; Ooi, K.; Katoh, S. *J. Colloid Interface Sci.* **1989**, *130*, 535.

(27) García-Martínez, O.; Rojas, R. M.; Vila, E.; Martín de Vidales, J. L. *Solid State Ionics* **1993**, *63-65*, 442.

(28) Martín de Vidales, J. L.; Rojas, R. M.; Vila, E.; García-Martínez, O. *Mater. Res. Bull.* **1994**, *29*, 1163.

Table 2. Tetragonal Cell Parameters (a, c), c/a' Ratio, Equatorial (d_{B-O}) and Axial ($d_{B-O'}$) Octahedral Bond Distances for $Mn_xCo_{3-x}O_4$, $x = 1.6$ and 1.8 , Quenched from 1000 °C

x	a (Å)	c (Å)	c/a'	d_{B-O} (Å)	$d_{B-O'}$ (Å)
1.6	5.8002(4)	8.6836(7)	1.058	1.995(4)	2.069(7)
1.8	5.7397(4)	8.9604(8)	1.104	1.959(4)	2.164(6)

The solids were centrifugated, washed with distilled water, and air-dried at 60 °C overnight. The concentrations of manganese and cobalt for all the samples studied as well as in the supernatant solutions were determined by atomic absorption spectroscopy with a Pye Unicam SP9 instrument.

X-ray powder diffraction diagrams were recorded at room temperature using a Siemens D-501 diffractometer with monochromatized Cu K α radiation. Diagrams were recorded in the step scanning mode, with a 0.025° (2θ) step scan and 2 s counting time. Divergence slits located in the incident beam were selected to ensure complete illumination of the specimen surface at 12° (2θ). The least-squares structure refinements were undertaken through the use of the Rietveld program DBWS-9006PC.²⁹ Rietveld refinements were made assuming space groups $Fd3m$ and $I4_1/amd$, for cubic and tetragonal spinel-type structures, respectively. For cubic $Fd3m$ spinels, 19 parameters were fitted to the 2801 data points as follows: 1 scale factor; 5 background parameters, 1 2θ zeropoint parameter, 6 profile function parameters (3 of them for the mixing parameter m , and 3 for the fwhm), 1 asymmetry correction parameter (for peaks below $2\theta = 50^\circ$), the cell parameter a , the oxygen positional parameter u , and 3 isotropic thermal parameters B , one for each Wyckoff equiposition 8a, 16d, and 32e. For tetragonal $I4_1/amd$ spinels, the same nonstructural parameters were refined, and the structural cell parameters a and c , the oxygen positional parameters $y(O)$ and $z(O)$ and 3 isotropic thermal parameters B , 1 for each equipoint (4a, 8d, and 16h) were also refined. Refinements were continued until the parameter shifts were less than 0.3 times the estimated standard deviations. Bond distances for cubic and tetragonal spinel oxides were deduced from a and u and from $a, c, y(O),$ and $z(O)$, respectively. Quantitative phase analysis has also been undertaken with the Rietveld method. It relies on the relationship³⁰

$$W_p = S_p(ZMV)_p / \sum_{i=1}^n S_i(ZMV)_i$$

where W_p is the relative weight fraction of phase p in a mixture of n phases, and $S, Z, M,$ and V are the Rietveld scale factor, the number of formula units per unit cell, the mass of the formula unit, and the unit cell volume (Å^3), respectively.

(29) Sakthivel, A.; Young, R. A. *Users Guide to Programs DBWS-9006 and DBWS-9006PC for Rietveld Analysis of X-ray and neutrons Powder Diffraction Patterns*; School of Physics, Georgia Institute of Technology, Atlanta, 1995.

(30) Hill, R. J.; Howard, C. J. *J. Appl. Crystallogr.* **1987**, *20*, 467.

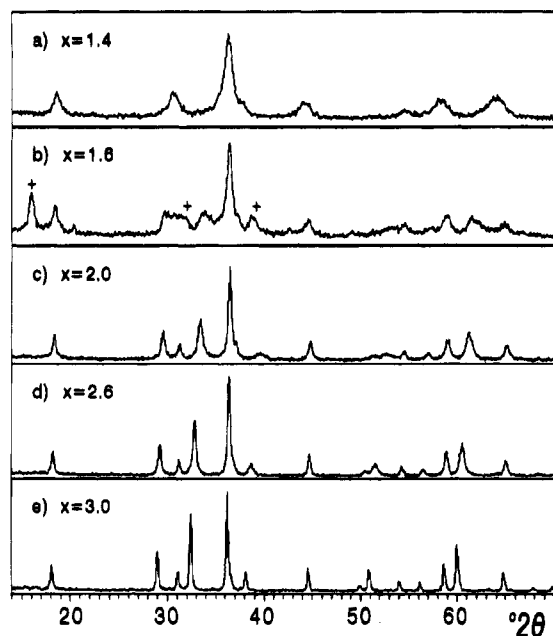


Figure 1. X-ray diffraction patterns of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ heated at 200 °C: (a) cubic spinel; (b) tetragonal spinel and $\text{Co}_8\text{O}_6\text{Cl}_4\cdot 7\text{H}_2\text{O}$ (+); (c–e) tetragonal spinels.

Results and Discussion

X-ray Powder Diffraction and Thermal Stability. (a) *Samples Cooled to Room Temperature.* In Figure 1, X-ray diagrams recorded for samples heated at 200 °C overnight are shown. For $x = 1.4$ the pattern is consistent with a cubic spinel-type structure (space group $Fd3m$) with cell parameter $a = 8.224(2)$ Å. For $x = 1.6$ a diagram with broad maxima assigned to a tetragonal spinel is obtained; moreover some additional diffraction maxima are observed. They are ascribed to cobalt oxide chloride hydrate $\text{Co}_8\text{O}_6\text{Cl}_4\cdot 7\text{H}_2\text{O}$ (JCPDS file 2-1119), which has also been synthesized by us by the procedure reported by Weiser and Milligan.³¹ Tetragonal cell parameters determined for the spinel indicate that we are dealing with an $x \approx 2$ phase (see Table 3), whose manganese content is higher than that in the original nominal composition; the excess of cobalt precipitates as $\text{Co}_8\text{O}_6\text{Cl}_4\cdot 7\text{H}_2\text{O}$. Diagrams recorded for samples $x = 2.0, 2.6,$ and 3.0 are presented in Figure 1c–e and are consistent with a tetragonal, spinel-type single phase, with distortion parameters 1.125, 1.150,

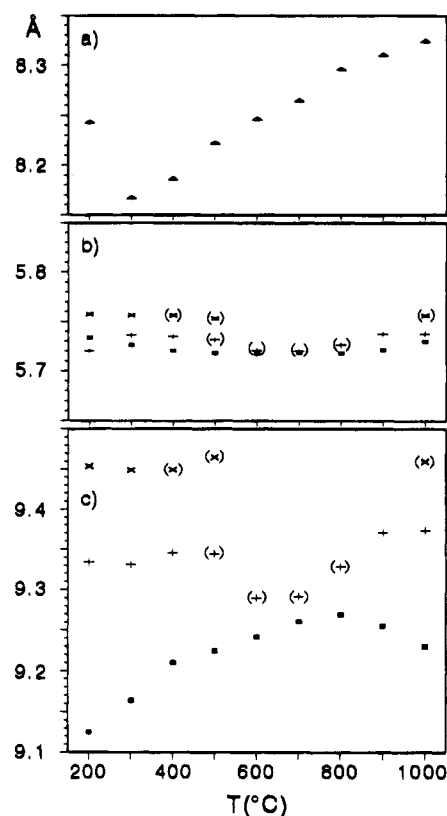


Figure 2. Variation with temperature of (a) cubic cell parameter a for the spinel $x = 1.4$; (b and c) tetragonal cell parameters a and c for spinels $x = 2.0$ (■), $x = 2.6$ (+), and $x = 3.0$ (×). Symbols in parentheses indicate the presence of a mixture of tetragonal spinel and bixbyite (see Table 1).

and 1.161, respectively. These results show that it is possible to obtain spinel-type materials, either cubic or tetragonal, at temperatures (200 °C) lower than those reported to date for the preparation of these oxides through ceramic^{14–16} or precursor methods.^{5,17}

To follow the transformations experienced by these oxides with temperature, batches of each sample were subjected to cumulative thermal treatments between 200 and 1000 °C. In Table 1 the phases identified and the distortion parameters for tetragonal phases observed at each temperature are summarized. In Figure 2 the variation of cell parameters for both cubic and tetragonal phases vs temperature is presented. Diagrams recorded for materials heated at 1000 °C are

Table 3. Results Obtained for the Original and Acid-Treated $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ Oxides (x and x' Stand for the Compositions before and after the Acid Treatment, Respectively)

samples before acid treatment				samples after acid treatment					
x	phases identified	cell parameters (200 °C)	cell parameters (1000 °C)	room temperature			heated at 1000 °C, 5 h		
				phases identified	cell parameters	proposed formula	phases identified	cell parameters	x'
1.00	C	8.215(4)	8.2509(2)	C	8.0923(9)	$(\square_{0.35}\text{Co}_{0.65})_A(\text{Mn}_{1.19}\text{Co}_{0.81})_B\text{O}_4$	C	8.3010(3)	1.35
1.40	C	8.224(2)	8.3216(3)	C	8.0930(9)	$(\square_{0.48}\text{Co}_{0.52})_A(\text{Mn}_{1.49}\text{Co}_{0.51})_B\text{O}_4$	C (23%) T (77%)	8.3149(5) 5.744(1)	1.77
1.60	C (58%) ^a T (42%)		8.3055(7) 5.7211(6) 9.210(1)	C	8.1077(9)	$(\square_{0.52}\text{Co}_{0.48})_A(\text{Mn}_{1.63}\text{Co}_{0.37})_B\text{O}_4$	C (3%) T (97%)	8.283(1) 5.7188(4) 9.2434(9)	1.98
2.00	T	5.7334(7) 9.125(1)	5.7296(6) 9.2304(9)	C	8.080(1)	$(\square_{0.68}\text{Co}_{0.32})_A(\text{Mn}_{1.77}\text{Co}_{0.23})_B\text{O}_4$	T	5.7265(3) 9.3048(6)	2.28
2.60	T	5.7202(4) 9.3340(8)	5.7375(2) 9.3734(4)	C	8.033(2)	$(\square_{0.92}\text{Co}_{0.08})_A(\text{Mn}_{1.97}\text{Co}_{0.03})_B\text{O}_4$	T	5.7486(1) 9.4267(3)	2.85

^a Percentages calculated from cell parameters at 1000 °C. At 200 °C there is a mixture of $\text{Co}_8\text{O}_6\text{Cl}_4\cdot 7\text{H}_2\text{O}$ and tetragonal spinel.

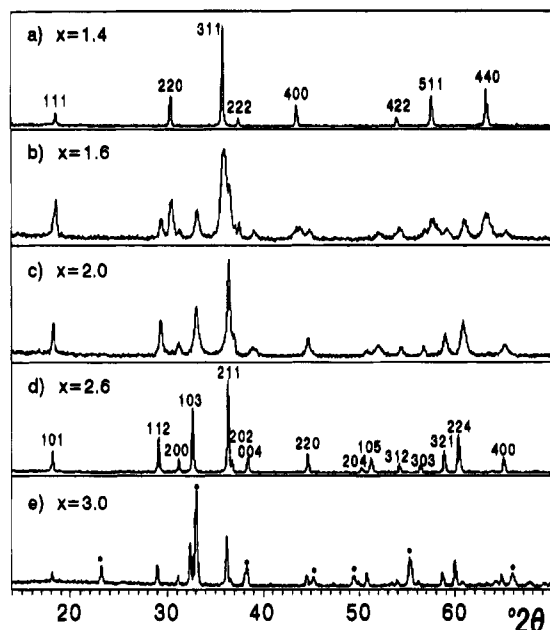


Figure 3. X-ray diffraction patterns of $Mn_xCo_{3-x}O_4$ heated at 1000 °C and cooled to room temperature within the furnace: (a) cubic spinel; (b) mixture of tetragonal and cubic spinels; (c and d) tetragonal spinels; (e) mixture of tetragonal spinel and bixbyite α - Mn_2O_3 (●). Cubic and tetragonal single phases are indexed.

shown in Figure 3. The more relevant results are presented below:

$x = 1.4$: the cubic cell constant sharply decreases from 8.224(2) at 200 °C to 8.168(2) Å at 300 °C (Figure 2a) and then steadily increases up to 8.3216(3) Å at 1000 °C. The contraction of the cell can be explained in terms of the oxidation of Mn^{3+} in B sites to Mn^{4+} . This result agrees with the data of Gillot,³² who has experimentally determined an oxidation temperature for Mn^{3+} in B sites of ≈ 280 °C. On the other hand, the regular increase of the cell constant up to 1000 °C can be regarded as a consequence of the progressive reduction of Co^{3+} to Co^{2+} and of Mn^{4+} in B sites to Mn^{3+} .¹⁹ In Figure 3a, the X-ray diagram of the cubic spinel-type phase formed at 1000 °C is shown; it is obtained as a single phase over the whole temperature range. This result allows us to enlarge the upper limit of the field of existence of the cubic spinel-type phase, from $x = 1.3$ ¹⁶ to $x = 1.4$.

$x = 1.6$: $Co_8O_6Cl_4 \cdot 7H_2O$ has disappeared at 400 and at 500 °C, the diffraction lines of the cubic spinel phase start to appear as well-defined maxima. A mixture of tetragonal and cubic spinels is formed starting at the latter temperature (Table 1), their relative amounts and cell constants varying with temperature; at 1000 °C (Figure 3b), the mixture contains 42% tetragonal ($x \approx 2$) and 58% cubic ($x \approx 1.3$).

$x = 2$: for cobalt manganite Mn_2CoO_4 , the tetragonal parameter a smoothly decreases as temperature increases to 800 °C and then increases from this temperature to 1000 °C (Figure 2b). The reverse, much more pronounced trend is observed for the tetragonal parameter c (Figure 2c). The smooth increase undergone by c between 200 and 800 °C can be justified in terms of the progressive reduction from Mn^{4+} to Mn^{3+} and from Co^{3+} to Co^{2+} . Between 800 and 1000 °C Mn^{3+} in B sites is reduced to Mn^{2+} and it moves to A sites, with the

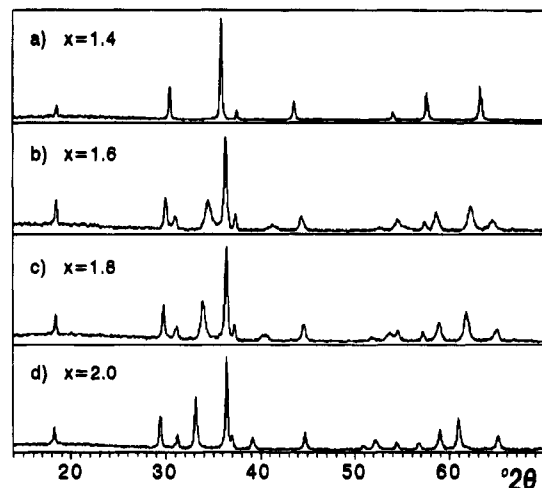


Figure 4. X-ray diffraction patterns of the spinel-type oxides $Mn_xCo_{3-x}O_4$ quenched from 1000 °C: (a) $x = 1.4$; (b) $x = 1.6$; (c) $x = 1.8$; (d) $x = 2.0$.

subsequent increase of the inversion parameter.¹⁴ Tetragonal distortion varies from 1.125 at 200 °C to 1.146 at 800 °C and diminishes to 1.139 at 1000 °C (Table 1). The pattern recorded for the sample heated at 1000 °C is shown in Figure 3c. It can be observed that the crystallinity of the spinel does not appreciably improve in going from 200 to 1000 °C.

$x = 2.6$: between 600 and 800 °C, $\approx 85\%$ bixbyite (α - Mn_2O_3) is segregated, and a mixture of bixbyite and a cobalt-enriched spinel is observed (Table 1), as shown by the rather large diminution of cell constants a and c (Figure 2b,c) of the tetragonal phase formed in this temperature interval. It is worth noting that a well-crystallized, spinel-like tetragonal single phase is obtained at 1000 °C (Figure 3d).

$x = 3$: between 400 and 500 °C, and at $T > 900$ °C, a mixture of tetragonal hausmannite (Mn_3O_4) and bixbyite exists. A very small increase of the tetragonal cell constants of hausmannite between 200 and 1000 °C, already reported in the literature,³³ is observed. Bixbyite is the only phase observed between 600 and 900 °C (Table 1).

(b) *Samples Quenched in Air.* As has been shown by Naka¹⁶ and is generally accepted, manganese cobalt oxides $Mn_xCo_{3-x}O_4$ obtained within the compositional range $1.3 < x < 1.9$, consist of a mixture of tetragonal and cubic spinels. However, Prokhvatilov and Gindin have described the formation in this compositional range, of a single phase with several tetragonal distortions³⁴ (JCPDS files 18-409 and 18-410). Having in mind these controversial data, we have considered it worthwhile to reinvestigate this region. Samples with $x = 1.4, 1.6, 1.8,$ and 2.0 were calcined to 1000 °C for 3 h and then quenched in air by rapidly removing them from the furnace. The X-ray diagrams recorded for quenched materials are presented in Figure 4.

Patterns recorded for $x = 1.4$ and 2.0 (Figure 4a,d) are similar to those presented in Figure 3a,c, the latter being recorded for samples with the same compositions, heated to 1000 °C and then slowly cooled to room

(31) Weiser, H. B.; Milligan, W. O. *J. Phys. Chem.* **1932**, *36*, 722.

(32) Gillot, B. *J. Solid State Chem.* **1994**, *113*, 163.

(33) Dorris, S. E.; Mason, T. O. *J. Am. Ceram. Soc.* **1988**, *71*, 379.

(34) Prokhvatilov, V. G.; Gindin, E. I. *Sov. Phys. Crystallogr.* **1965**, *10*, 191.

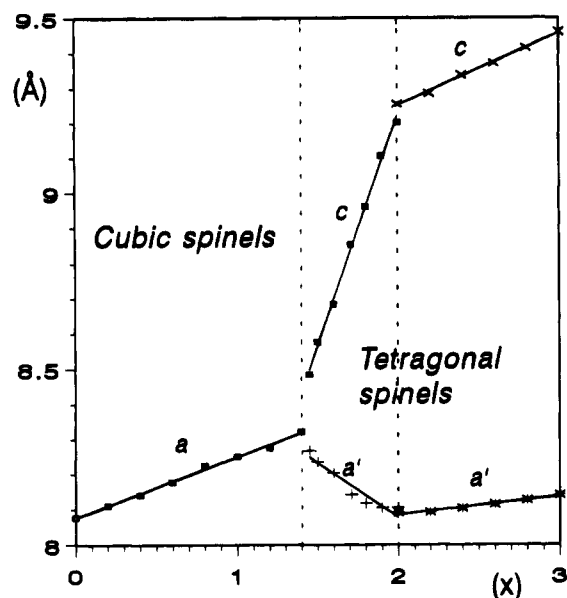


Figure 5. Variation of the experimental lattice constants vs composition (x) for phases identified in the $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ ($0 \leq x \leq 3$) system. Data correspond to samples heated at 1000°C ; samples in the compositional range $1.4 < x < 2.0$ were quenched from this temperature ($a' = a\sqrt{2}$).

temperature. However, for $x = 1.6$ and 1.8 (Figure 4b,c), X-ray powder diagrams show that the mixture of tetragonal and cubic spinel-like oxides above reported is no longer formed (Figure 3b); instead, patterns can be fully indexed on the basis of a tetragonal cell (space group $I4_1/amd$) with lattice constant c rather smaller than that determined for Mn_2CoO_4 ($x = 2.0$). Experimental lattice constants, distortion parameter ca' , and equatorial (d_{B-O}) and axial ($d_{B-O'}$) octahedral bond distances for $x = 1.6$ and 1.8 are summarized in Table 2. The tetragonal parameter c increases from $8.6836(7)$ Å for $x = 1.6$ to $8.9604(8)$ Å for $x = 1.8$, whereas a goes from $5.8002(4)$ to $5.7397(4)$ Å. On the other hand, it is worth mentioning that the differences between the axial and equatorial bond lengths appreciably increase with x . These results point to the formation of a tetragonal, spinel-like single phase, for the oxides $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ ($1.4 < x < 2.0$), and clearly show that the amount of Mn^{3+} in octahedral B sites increases with x , that is, the inversion spinel parameter decreases.

Solid Solutions in the $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ ($0 \leq x \leq 3$) System. In Figure 5, the evolution of the experimental values for the lattice constants for phases identified in the system $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ in the compositional range $0 \leq x \leq 3$, is depicted. Three zones can be clearly differentiated:

$0 \leq x \leq 1.4$: data presented are determined from materials heated at 1000°C and allowed to slow cool within the furnace. A cubic, spinel-type solid solution is formed as a single phase; its lattice constant steadily increases from $8.0769(2)$ Å ($x = 0$, Co_3O_4) to $8.3216(3)$ Å ($x = 1.4$).

$2.0 \leq x \leq 3.0$: the same trend is observed for cell parameters a and c corresponding to the tetragonal solid solution formed for materials heated at 1000°C and slowly cooled within the furnace. The range is from $a = 5.7296(6)$, $c = 9.2304(9)$ Å to $a = 5.7561(2)$, $c = 9.4599(2)$ Å.

$1.4 < x < 2.0$: samples were quenched in air from 1000°C . A tetragonal solid solution is formed as a

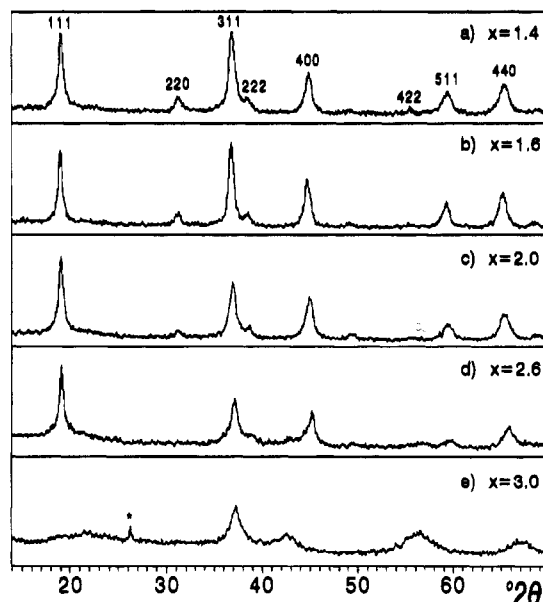


Figure 6. X-ray diffraction patterns of samples $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ with $x = 1.4, 1.6, 2.0, 2.6$, and 3.0 , heated at 200°C and treated with 0.25 M HCl for 24 h. Diagrams a–d correspond to cubic spinels; (e) corresponds to a mixture of $\epsilon\text{-MnO}_2$ and $\text{MnO}(\text{OH})$ (*) (see Table 3).

single phase over this compositional interval. The tetragonal lattice constant a decreases from $5.8455(4)$ ($x = 1.45$) to $5.7305(5)$ Å ($x = 1.9$), while c increases from $8.4843(6)$ to $9.106(1)$ Å for the same compositions. However, if these materials are cooled within the furnace, a mixture of a tetragonal phase with $x \approx 2$ and a cubic phase with $x \approx 1.3$ is always obtained, their relative amounts depending on the composition of the starting material. A more detailed study of this compositional range is currently being carried out.

It is worth mentioning that the formation of a tetragonal single phase in the range $1.4 < x < 2.0$ is here reported for the first time; the only previous reference to a similar material is that of Prokhvatilov and Gindin,³⁴ who report the formation of an "intermediate tetragonal spinel structure between MnCo_2O_4 (cubic) and Mn_3O_4 (tetragonal)".

The variation of cell parameters (Figure 5) show that Vegard's rule holds for each of the three well-defined compositional ranges. Consequently, the existence of three well differentiated solid solutions in the $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ ($0 \leq x \leq 3$) can be established.

Reactivity in Acid Medium. The acid-treated samples were prepared by soaking $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ ($1 \leq x \leq 3$) oxides heated at 200°C , in 200 mL of a 0.25 M HCl solution. The supernatant liquid showed a pale-pink color, indicating the presence of Co^{2+} in the solution. Atomic absorption data show that manganese and cobalt are present in the solution.

In Figure 6, X-ray powder diffraction diagrams are shown for acid-treated samples with original compositions $x = 1.4, 1.6, 2.0, 2.6$, and 3.0 . From a comparison between these patterns and those presented in Figure 1, which correspond to the original untreated samples, the following results arise:

(i) Starting composition $x = 1.4$: the cubic spinel structure is maintained; however, the intensity ratio I_{111}/I_{311} dramatically increases after acid treatment, and

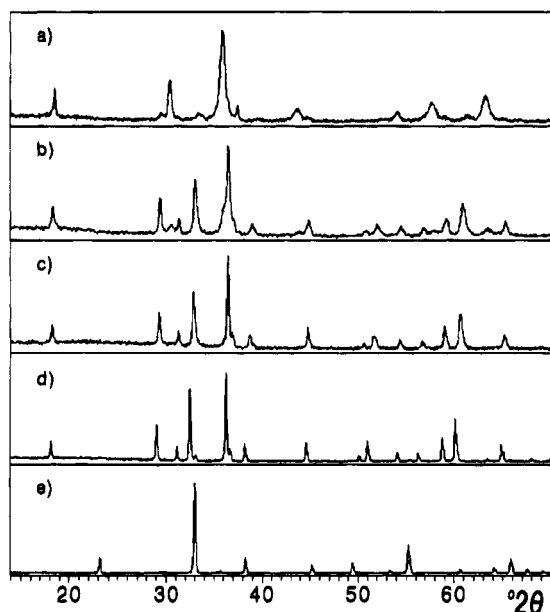


Figure 7. X-ray diffraction patterns of the acid-treated samples with original compositions $x = 1.4, 1.6, 2.0, 2.6,$ and 3.0 , heated at $1000\text{ }^{\circ}\text{C}$ for 5 h (see Table 3).

the cell parameter diminishes from $8.224(2)$ to $8.0930(9)\text{ \AA}$.

(ii) Starting compositions $x = 1.6\text{--}2.6$: the acid-soaking treatment induces the transformation of the tetragonal spinel-type phases into the cubic spinel-type structure; the intensity ratio I_{111}/I_{311} in the new-formed cubic spinels increases with x .

(iii) For hausmannite, Mn_3O_4 ($x = 3$), a mixture of $\epsilon\text{-MnO}_2$ and $\text{MnO}(\text{OH})$ (JCPDS files 30-820 and 41-1379, respectively) is identified.

(iv) The intensity of the (220) diffraction line for cubic phases formed after acid treatment decreases with x , and it vanished for $x = 2.6$.

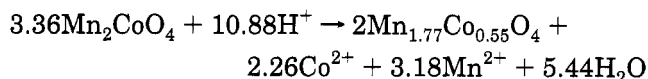
Table 3 shows the phases identified and their cell parameters for materials before and after acid treatment; they have been determined from the Rietveld refinement method.

To determine the compositions, the acid-treated materials were heated to $1000\text{ }^{\circ}\text{C}$ for 5 h and then allowed to slow cool within the furnace; X-ray diffraction patterns recorded at room temperature are shown in Figure 7. Phases identified and corresponding cell constants are gathered in Table 3. Interpolation in Figure 5 of the experimental cell parameters allows us to determine the compositions, that is, the x' values of the new spinel-like oxides. They agree with Co/Mn ratios determined by atomic absorption. From these x' values and from cobalt content in A sites as determined by the Rietveld method, the formulas for the acid-treated materials formed at room temperature can be derived. They are also presented in Table 3. It can be observed that the amount of cobalt in tetrahedral coordination decreases from 0.65 ($x' = 1.35$) to 0.08 ($x' = 2.85$).

It is worth noting that the cubic cell parameter of the acid-treated spinels with original composition $x = 2.6$ ($8.033(2)\text{ \AA}$) is identical to that reported for $\lambda\text{-MnO}_2$ ($a = 8.03\text{ \AA}$).²² Having in mind the low cobalt content (3.2%) of the acid-treated phase, it can be regarded as $\lambda\text{-MnO}_2$.

Bertaut³⁵ has pointed out that the intensity of reflection (220) depends only on the scattering power of the ions in tetrahedral A sites, while the intensity of the (440) reflection mainly depends on the scattering power of ions in octahedral B sites. The presence of the (220) reflection in the patterns of the cubic spinel obtained from the acid-treated materials with original compositions $x = 1.4, 1.6,$ and 2.0 (Figure 6a–c) shows that some cobalt ions are located in the tetrahedral sites of the cubic close-packed oxygen framework, whereas this reflection is not observed for material $x = 2.6$ (Figure 6d), meaning that the amount of cobalt ions in A sites is not significant, as it has been confirmed by Rietveld refinement. Mn^{3+} ions in B sites disproportionate to Mn^{4+} and Mn^{2+} . Mn^{2+} and the Co^{2+} extracted from A sites dissolves, while Mn^{4+} in B sites gives way to the topotactic formation of the cubic cobalt-deficient spinel-like oxides.

From these results, the formation of cobalt-deficient manganites can be accounted for on the basis of a redox-type mechanism, analogous to that proposed by Feng et al.²³ for LiMn_2O_4 . It can be *ideally* expressed, as an example for $x = 2$, as follows:



However, the assumption that the oxidation states of manganese and cobalt in the original spinels heated at $200\text{ }^{\circ}\text{C}$ are Mn^{3+} and Co^{2+} , should be taken with caution.

A detailed study of the influence of the temperature of treatment of the original cobalt manganese spinel precursors, the acid concentration and the length of acid treatment, on the properties of the acid-treated materials is presently being carried out.

Conclusions

The synthesis procedure used here for the preparation of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$, $1 \leq x \leq 3$, affords highly reactive materials with many potential applications. The existence of a cubic and two tetragonal solid solutions for $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ in the compositional range $0 \leq x \leq 3$ has been established, and their field of existence has been delimited. On the other hand, acid treatment of cobalt manganese spinels obtained at $200\text{ }^{\circ}\text{C}$ yields cobalt-deficient manganese spinels or $\lambda\text{-MnO}_2$, depending on the compositions of the original oxides. The potential of the new oxides as raw materials for Li^+ insertion/extraction reactions in aqueous media is being explored.

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(35) Bertaut, F. *C.R. Acad. Sci. Paris* **1950**, *230*, 215.

(36) Feng, Q.; Kanoh, H.; Miyai, Y.; Ooi, K. *Chem. Mater.* **1995**, *7*, 379.