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Mn, Co OXIDES PREPARED BY THE THERMAL DECOMPOSITION OF CARBONATES

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ABSTRACT

Mixed Mn,Co carbonates of general formula $Co_{1-x}Mn_xCO_3$ (x=0.33, 0.5, 0.66) are used as precursors in the preparation of mixed oxides with rock-salt and spinel structures. The thermal decomposition of the precursors in air leads to cation-deficient spinels with O/M ratios close to 1.5 that are progressively reduced to M_3O_4 with increasing temperature. The decomposition in inert atmosphere leads to mixed monoxides, which are partially oxidized, especially those which are Mn containing. The values of $\underline{a}$ of the rock-salt phases increase with Mn content. The solid is composed of small domains of anisotropic sizes.

INTRODUCTION

The preparation of inorganic solids by the thermal decomposition of precursor compounds is a straightforward procedure to obtain new oxide phases. This fact was recently shown in the Ca-Mn-O [1] and Ca-Fe-O [2] systems by using calcite-type mixed carbonates. Additionally, carbonate precursors may also be used in the preparation of highly-dispersed mixed-oxide particles [3] with good homogeneity in composition.

On the other hand, due to the multiple oxidation states and structural possibilities, the mixed oxides in the Co-Mn-O system are numerous and their complex relationships are demonstrated in the equilibrium phase diagrams [3,4]. Additionally, the preparation of some of these compounds under non-equilibrium conditions may lead to wide ranges of non-stoichiometry, specially in those phases with defect assimilation possibilities as rock-salt and spinel phases. The use of carbonate precursors may be of interest to prepare non-equilibrium metastable phases with high homogeneity in cation distribution.

In this work, calcite-type Mn, Co carbonates are coprecipitated and their low-temperature decomposition is studied, with special emphasis on the

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characterization of the resulting monoxides and spinel related phases.

EXPERIMENTAL

Mixed carbonates of general formula $Co_{1-x}Mn_xCO_3$ were prepared from the addition of a 1.0 M solution of $NaHCO_3$ to a 0.5 M solution of Co(II) and Mn(II) in the desired proportions, while continuously passing CO_2. Mn and Co contents were determined by atomic absorption spectrometry. The homogeneity in cation distribution was confirmed by electron microprobe X-ray ED analysis. The oxygen content of the samples was determined by dissolving the solid in the presence of Fe(II) in inert atmosphere and back-titrating with $K_2Cr_2O_7$.

X-Ray diffraction was carried out with a Siemens D500 diffractometer working with CuK_α radiation monochromated by a graphite crystal. The X-ray line profiles used in intensity measurements, precision determination of lattice parameters and line-broadening analysis were recorded by step-scan with step sizes of 0.02°2Θ. Si was used as standard in these analysis. Crystallite size and microstrains were computed by profile fitting to Pearson-VII functions.

DSC traces were obtained with a Mettler TA 3000 apparatus under dynamic Ar and static air atmospheres. TG traces were recorded with a Cahn 2000 electrobalance under static air atmosphere.

RESULTS AND DISCUSSION

All the Mn,Co mixed carbonates obtained by coprecipitation had calcite-like structures and their X-ray diffractograms showed no other diffraction lines. Table 1 shows the experimentally determined values of x in the general formula $Co_{1-x}Mn_xCO_3$. These values are close to the cation proportions of the starting solutions. The x values determined in the different oxides prepared from these carbonates were also coincident. The distribution of Co and Mn in the various solids was homogeneous, at least within the experimental limits of the electron microprobe.

The DSC (Fig. 1 a-d) and TG (Fig. 2) traces of the carbonates, recorded in static air atmosphere show a complex thermal effect developing between 300 and 400°C, depending on the value of x. In this effect the endothermic carbonate decomposition is accompanied by a partial oxidation of exothermal nature. The products obtained at different temperatures after the decomposition process in air show spinel-type structures as shown by X-ray diffraction. However, the solids prepared at low-temperatures (400 and 600°C) show high O/(Mn+Co) ratios (Table 1) that depart markedly from the M_3O_4 stoichiometry. In fact, between 400 and 600°C these are close to an γ-M_2O_3 phase. In some

TABLE 1

Chemical and structural properties of defective spinel phases prepared by the thermal decomposition of mixed carbonates at 400 and 600°C.

	400°C			600°C		
x ($Co_{1-x}Mn_x$)	O/M	a(Å)	I_{220}/I_{400}	O/M	a(Å)	I_{220}/I_{400}
1.000	1.603	T	T	1.583	T	T
0.681	1.599	T	T	1.503	T	T
0.528	1.550	8.183	0.555	1.510	8.355	1.044
0.375	1.529	8.151	0.666	1.462	8.300	1.309
0.000	1.303	-	-	1.362	-	-

T, Tetragonal phase.

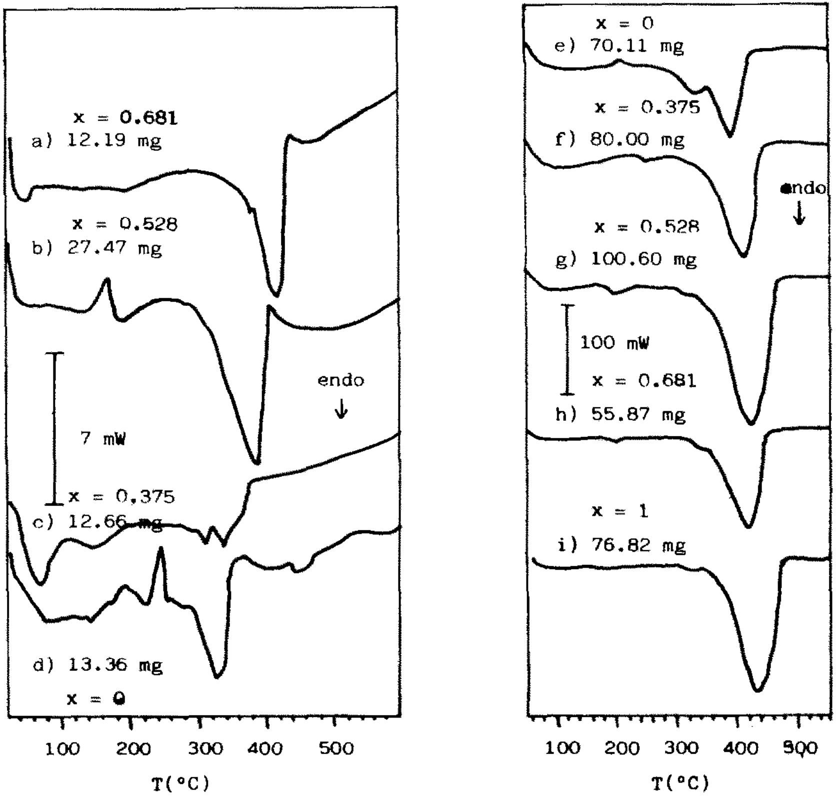

Fig. 1. DSC traces of $Co_{1-x}Mn_xCO_3$ recorded in static air (a-d) and dynamic Ar (e-i) atmospheres.

cases, the O/(Mn+Co) ratio is higher than 1.5. These values may be interpreted by assuming the presence of manganese compound with Mn in oxidation states higher that 3, which are undetectable by X-ray diffraction, or by considering that Mn(IV) is present in the defective spinel structure, thus originating a high level of cation vacancies in the solid. In this respect, it is worth noting that Mn(IV) has been iddentified in defective Fe,Mn spinels [6] and that some Ti(IV)-containing, Co-spinels and ferrites reach O/M ratios higher than 1.5, as $(Fe^{+3})_A(Fe^{+3}Ti^{+4}_{0.5}\square_{0.5})_B O_4$ [7].

On the other hand, the distribution of vacancies in the defective spinels obtained by the precursor method in the Co-Mn-O system was analysed from the experimental I_{220}/I_{400} ratios, according to the assumptions in [8]. These ratios were determined in those samples where the tetragonal distortion of the spinel structure was negligible (Co/Mn = 1, see Table 1) and are intermediate between those calculated for all vacancies in A-sites (0.46) and B-sites (1.96). However, at 400°C they are closer to those expected for tetrahedral vacancies, while a significant redistribution is observed at 600°C that accounts for a higher level of octahedral vacancies. The presence of Mn(IV) and Co(III) ions agrees well with a high tendency to occupy octahedral positions. From 600 to 900°C, the TG traces (Fig. 2) show a continuous weight loss until the M_3O_4 stoichiometry free of cation vacancies is reached between 900 and 1000°C, depending on the value of x.

According to the TG diagrams in Fig. 1, the occurrence of (Co,Mn)O phases is expected at temperatures higher than 900-1000°C in air atmosphere. However, the thermal decomposition of carbonate precursors allows the formation of monoxide phases with high homogeneity in composition when carried out under inert atmosphere at low temperatures. To achieve this preparation, the decomposition products need to be cooled to room temperature under the same inert conditions to avoid oxidation to spinel phases. The DSC traces recorded in this atmosphere are also included in Fig. 1 and show a less-complex effect of endothermal nature, corresponding to carbonate decomposition exclusively. The materials obtained by this procedure were rock-salt phases, as shown by X-ray diffraction. Occasionally (as in x=1), the diffractograms showed the presence of weak lines ascribed to spinel-structure phases. The origin of the partial oxidation is not clear. New DSC experiments were carried out in N_2, Ar and CO_2 dynamic atmospheres and a variable spinel content was found. The possibility that these gases contain O_2 traces that may be responsible of the oxidation cannot be discarded.

The chemical and structural properties of the oxides obtained after the DSC runs in Ar atmosphere are shown in Table 2. From the O/M ratios, it is worth noting that those samples with x>0 have high oxygen contents, probably

TABLE 2

Chemical and structural data of partially-oxidized rock-salt monoxides obtained by the thermal decomposition of mixed carbonates in Ar atmosphere.

x ($Co_{1-x}Mn_x$)	O/M	$\underline{a}$(Å)	D_{111}(Å)	$\tilde{e}_{111}(\cdot 10^3)$	D_{220}(Å)	$\tilde{e}_{220}(\cdot 10^3)$
1.000	1.131	4.446	5000	2.2	908	1.2
0.681	1.118	4.375	620	2.1	259	1.4
0.528	1.127	4.352	770	3.8	522	3.7
0.375	1.224	4.316	407	2.9	257	3.4
0.000	1.032	4.263	360	0.7	486	1.4

D: volume averaged crystallite size

ẽ: Microstrains content

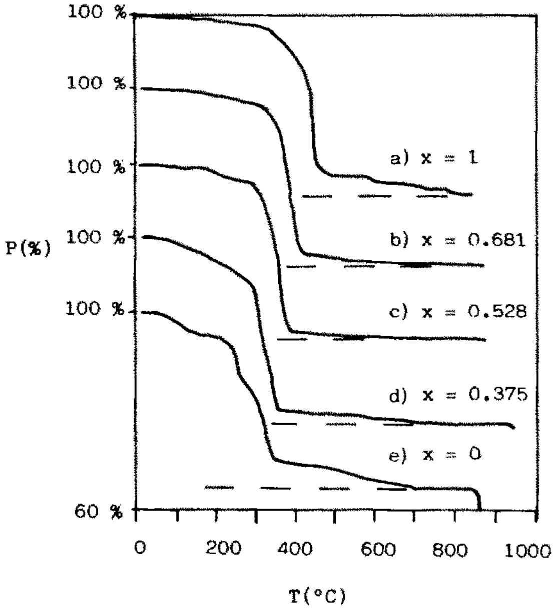

Fig. 2. TG traces of $Co_{1-x}Mn_xCO_3$ recorded under static air atmosphere.

indicating a higher density of clustering in the Mn-rich phases. The lack of a continuous relationship between O/M and x was also found in Mn,Fe monoxides [9]. The rock-salt unit cell parameter a increases gradually with x, as expected.

The degree of imperfection in these solids was evaluated by the X-ray line broadening analysis in two crystallographic directions. The values of crystallite size (D) and microstrains ($\tilde{e}$) obtained from this analysis are also included in Table 2. These parameters are highly anisotropic, indicating a non-regular shape of the coherently diffracting domains. These domains have small size except for x=1 but show little dependence upon the values of x. The fact that the oxides prepared by the precursor method have a high degree of dispersion and a high homogeneity in cation distribution may condition their physico-chemical applications, as these properties are difficult to obtain simultaneously.

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