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Journal of Alloys and Compounds 434–435 (2007) 816–819

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Structural and microstructural characterization of Co-hydrotalcite-like compounds by X-ray diffraction

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Available online 17 October 2006

Abstract

Co-hydrotalcite-like compounds (Co-HTlcs) were synthesized by coprecipitation technique from $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$, with a constant molar ratio Mg/Al of 1.6 and a variable molar ratio Co/Mg from 0.01 to 0.1 (controlling the pH around 10). X-ray diffraction was used to evaluate structural (lattice parameters) and microstructural (crystallite size and microstrain) parameters of the samples. Lattice parameters were calculated from (0 0 3), (0 0 6), (1 1 0) and (1 1 3) reflections by the least squares method, changes on *a* and *c* lattice parameters are discussed and related to Co/Mg ratio. The microstructural parameters were analyzed using two approaches: (a) *analytical methods* with the Voigt method and the two stages approach and (b) *graphical methods* using a modified Williamson–Hall plot with Lorentzian, Gaussian and Lorentzian–Gaussian variants. It was found that increasing the Co content, the morphology of crystallites tends to be plate-like and it was observed that the crystallite size increases, while the microstrain values decrease. This behavior is related to an improvement of crystal perfection, due to addition of cobalt.

Keywords: Nanostructures; Precipitation; X-ray diffraction

1. Introduction

Hydrotalcite-like compounds (HTlcs) have received considerable attention in recent decades due their applications related to heterogeneous catalysis, these materials exhibiting properties of high surface area and reactivity [1–4]. It is well known that microstructural defects influence many electrical, optical, chemical and catalytic properties [5]; an important application of X-ray powder diffraction is the use of profile broadening to evaluate microstructural features such as the crystallite size and microstrain [6]. Characterization of solids in terms of their microstructure is required in several fields of materials science such as reactivity of solids, catalysis, solid-state reactions. The microstructural characterization by means of X-ray diffraction of HTlcs has been commonly performed for crystallite size [4,7–9] with no instrumental correction, but the microstrain contribution usually is neglected. The aim of the present work is to show the application of a methodology in order to characterize the size and strain of HTlcs being replaced with Co in an increasing ratio.

2. Experimental

2.1. Synthesis

Co-hydrotalcite-like compounds (Co-HTlcs) were synthesized by coprecipitation of an aqueous solution of $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ at room temperature and continuous stirring, with a constant molar ratio Mg/Al of 1.6 and a variable molar ratio Co/Mg from 0.01 to 0.1. The pH was controlled around 10 using NaOH and Na_2CO_3 as the precipitant agent. After the addition process, the slurry was continuously stirred for 1 h with the purpose of maintaining the homogeneity of the sample. The suspension was aged about 16–18 h at room temperature, washed, filtered and finally dried during 10 h at 120 °C. Table 1 shows the Co-HTlcs samples prepared and their composition.

2.2. Characterization by X-ray diffraction

The samples were analyzed using an X-ray powder diffractometer, Siemens D500 with Co Kα radiation (1.7889 Å) and diffracted beam graphite monochromator, as follows: samples of Co-HTlcs were measured from 5° to 90° in 2θ, step size of 0.02° and counting time of 5 s step^{-1}. Annealed ZnO strain-free with

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doi:10.1016/j.jallcom.2006.08.204

Table 1
Samples nomenclature and compositions

Sample	Co content (mol%)	Co/Mg ratio
MHS-9	0.9	0.010
MHS-10	1.7	0.019
MHS-12	5.2	0.058
MHS-13	6.9	0.077
MHS-14	8.6	0.096

crystallite size up 5 μm, was measured in order to obtain data for instrumental contribution to broadening, from 30° to 140° in 2θ, with step size 0.01° and counting time 5 s step^{-1}.

These data were used for phase identification, structural (lattice parameters calculations) with a general least squares method [10], and microstructural parameters characterization (crystallite size and microstrain).

Microstructural features were studied by—(a) analytical methods: the Voigt method and the two stages approach [5,6,11,12]; (b) graphical approaches: Williamson–Hall type plots in Lorentzian, Gaussian and Lorentzian–Gaussian variants [13].

For analytical methods, calculations used to obtain instrumental broadening were based on whole pattern procedure with Fullprof software [14]. Sample broadening and other profile measurements as angular position, and also profile shape parameters were obtained with pattern decomposition subroutine using Winplotr software [15]. In both cases, a pseudo-Voigt function was considered to perform the profile fitting.

In the case of graphical methods, a worksheet was developed in order to determine the maximum of intensity angular position and integral breadth which was calculated by numerical integration with no assumption of a specific profile function.

3. Results and discussion

3.1. X-ray diffraction

Diffractograms of the Co-HTlcs are shown in Fig. 1. All samples crystallized only in a pure hydrotalcite-type phase (JCPDS 14-191).

3.2. Lattice parameters

Estimation of a and c lattice parameters were calculated from a least squares method taking reflections (0 0 3), (0 0 6), (1 1 0) and (1 1 3), and the cell volume was calculated, they are presented in Table 2 as function of Co content.

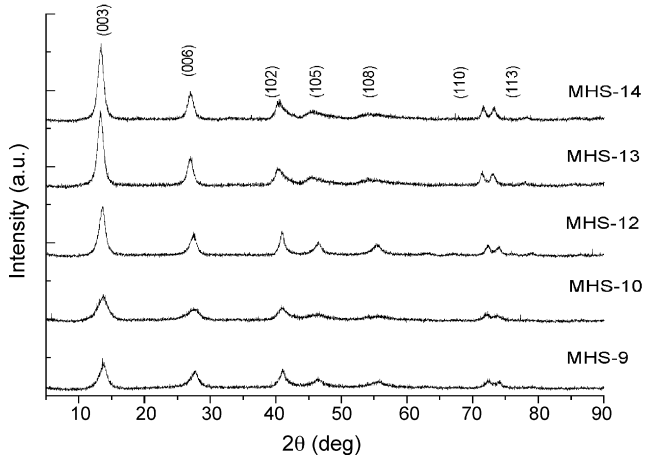

Fig. 1. X-ray diffractograms for synthesized Co-HTlcs.

Table 2
Lattice parameters results

	MHS-9	MHS-10	MHS-12	MHS-13	MHS-14
a (nm)	0.3020	0.3042	0.3036	0.305	0.306
c (nm)	2.253	2.256	2.268	2.307	2.301
Volume (nm^3)	0.179	0.181	0.1816	0.186	0.187

Table 3
Parameters for both instrumental broadening and profile shape

U	0.027279
V	−0.054322
W	0.05057
η_0	0.15412
X	0.006382

There is a small increase on the a lattice as Co/Mg ratio increases, which can be negligible; however, it is observed a notable change related to c lattice. In general, the cell size increased with addition of Co, this can be observed in changes of volume cell. It was expected that a parameter varies mainly with cation nature and c with anion and interlayer; however, in this study a lattice parameter did not exhibit considerable changes, and hence it, can be inferred that distortion ought to be observed in basal planes and higher strain should occur along c axis.

3.3. Size and strain

3.3.1. Analytical methods

Instrumental profile. Data obtained from whole pattern fitting for ZnO are shown in Table 3. The parameters U, V and W are related to the full width at half maximum (FWHM) in the Caglioti's formula [12]:

$$\text{FWHM} = \sqrt{U\tan^2\theta + V\tan\theta + W} \quad (\theta \text{ in rad}) \tag{1}$$

η_0 and X model the trend of the pseudo-Voigt mixing parameter η, used in the profile fitting [11,12]:

$$\eta = \eta_0 + X2\theta \quad (2\theta \text{ in } ^\circ) \tag{2}$$

Voigt method. Results of calculations are shown in Tables 4 and 5 as crystallite size and strain dependence as function of cobalt content. In general, the size increased with cobalt content, showing an anisotropic behavior. Size related to (0 0 3)

Table 4
Results from analytical methods for crystallite size dependence (nm)

Sample	Voigt method		Two stages approach	
	(0 0 l)	(h h 0)	(0 0 l)	(h h 0)
MHS-9	5.10	11.90	5.61	12.79
MHS-10	4.49	8.36	4.46	8.36
MHS-12	7.69	14.45	7.62	14.38
MHS-13	9.32	20.72	9.23	20.63
MHS-14	9.55	17.06	9.47	16.99

Table 5
Results from analytical methods for microstrain dependence

Sample	Voigt method		Two stages approach	
	(0 0 *l*)	(*h h* 0)	(0 0 *l*)	(*h h* 0)
MHS-9	0.0099	0.0034	0.0089	0.0026
MHS-10	0.0289	0.0026	0.0289	0.0026
MHS-12	0.0146	0.0024	0.0147	0.0029
MHS-13	0.0148	0.0020	0.0148	0.0020
MHS-14	0.0143	0.0019	0.0143	0.0020

Table 6
Results from graphical methods for crystallite size dependence

Sample	Lorentzian (Cauchy)		Gaussian		Gaussian–Lorentzian	
	(0 0 *l*)	(*h h* 0)	(0 0 *l*)	(*h h* 0)	(0 0 *l*)	(*h h* 0)
MHS-9	6.92	–	5.12	–	–	112.5
MHS-10	7.51	–	5.25	–	–	2.11
MHS-12	8.97	–	7.13	–	–	3.64
MHS-13	10.19	–	7.84	–	–	3.72
MHS-14	18.71	–	9.46	–	–	4.06

and (0 0 6) reflections named as (0 0 *l*) is always smaller than for (1 1 0), named (*h h* 0), and the difference increases with cobalt content, which indicates that the geometry of the particle changes its shapes, becoming flattened at higher amounts of cobalt. Strain dependence is shown in Table 5, it is observed that microstrain decreases with molar cobalt content and the value is lower for (*h h* 0) than for (0 0 *l*) reflections.

Two stages approach. Results are in close agreement with those for the Voigt method, the crystallite size increases and the strain decreases as the cobalt content is increased, and it is observed an anisotropic behavior on crystallite size and microstrain with the greater values are related to (*h h* 0) and (0 0 *l*) reflections, respectively.

This behavior in microstructural parameters means that, by increasing the cobalt content in the sample, the crystal perfection is also improved by increasing crystallite size and decreasing microstrain.

3.3.2. Graphical methods

Plots for Lorentzian and Gaussian approaches for (0 0 *l*) reflections are shown in Fig. 2. They show the presence of small crystallite size and microstrain, numerical values obtained from the plots (Lorentzian–Gaussian is not shown) being given in Table 6 for crystallite size dependence and in Table 7 for microstrain dependence on cobalt content.

Lorentzian plot. In the (0 0 *l*) family of reflections increases size but the microstrain values can be considered as constant, for (*h h* 0) reflections the results are associated to an infinite size and the microstrain decreases. Commonly the Cauchy (Lorentzian) profile is associated to crystallite size effect, and it is expected that the results from this plot will be in agreement with analytical results, which it is not the case.

Gaussian plot. Results for crystallite size in (*h h* 0) reflections can be considered as infinite, and for (0 0 *l*) increase with cobalt content. The microstrain decreases with as cobalt content increases for (0 0 *l*) reflections, while it can be assumed constant for (*h h* 0) reflections, this behavior being in agreement with the results obtained with analytical methods; in consequence, the estimation of size and strain by a Gaussian plot is more reliable than using a Lorentzian plot for the studied samples.

Lorentzian–Gaussian plot. Results for crystallite size related to (0 0 *l*) reflections can be considered of infinite size while for (*h h* 0) reflections decrease as the cobalt content increases. The shape of the crystallite is almost the same as obtained with analytical and the other graphical methods, however the direction of growth is the opposite, this result is very critical, because the catalytical properties are dependent on crystal directions. Microstrains are absent on (*h h* 0) reflections and for (0 0 *l*) reflections there is no clear trend associated to cobalt content. In general, the microstructural features evaluated show an irregular behavior to that obtained with the analytical and the other graphical methods. The results obtained from this plot are inconsistent.

In the case of HTlcs, the main feature observed is the small crystallite size rather than the microstrain effect, which could be the reason that Lorentzian–Gaussian plot showed a critical deviation from the other methods.

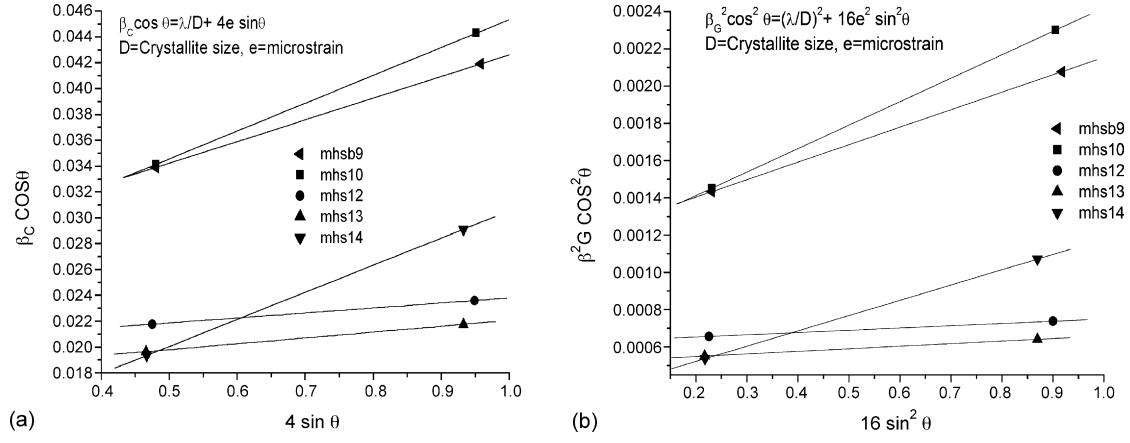

Fig. 2. Lorentzian (a) and Gaussian (b) Williamson–Hall plots type for (0 0 l) reflections.

Table 7
Results from graphical methods for microstrain dependence

Sample	Lorentzian (Cauchy)		Gaussian		Gaussian–Lorentzian	
	(0 0 *l*)	(*h h* 0)	(0 0 *l*)	(*h h* 0)	(0 0 *l*)	(*h h* 0)
MHS-9	0.0042	0.0182	0.0076	0.0030	0.0333	–
MHS-10	0.0053	0.0207	0.0068	0.0036	0.1121	–
MHS-12	0.0009	0.0169	0.0050	0.0027	0.1124	–
MHS-13	0.0011	0.0117	0.0041	0.0029	0.0894	–
MHS-14	0.0052	0.0139	0.0041	0.0034	0.0424	–

4. Conclusions

Pure Co-HTlc nanocrystalline phase was obtained. Addition of cobalt increases the crystal perfection due to increasing crystallite size and decreasing microstrain.

A distortion in the cell can be detected at lower amounts of cobalt as a high value of microstrain along [0 0 l], and at higher values as increase of *c* lattice parameter. The presence of microstrain should not be discarded in the microstructural studies for HTlcs.

Analytical methods had more reliability than graphical approaches, however, the use of Gaussian plot can give a close approximation in the case of Co-HTLcs. For evaluating microstructural parameters the Lorentzian–Gaussian plot is not suitable.

Acknowledgement

This work has been supported by COFAA-IPN and CGPI-IPN.

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