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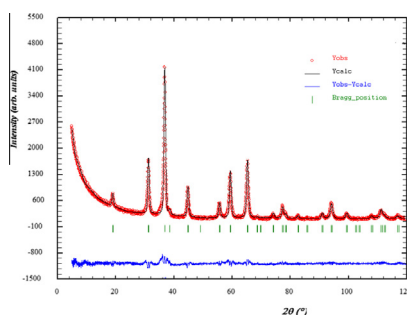
The decomposition of the layered double hydroxides of Co and Al: Phase segregation of a new single phase spinel oxide

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HIGHLIGHTS

- The Rietveld refinement of Co–Al–CO₃ hydroxalcite.
- Infrared and Raman spectroscopy of Co–Al–CO₃ hydroxalcite.
- The Rietveld refinement of the oxide product.
- Infrared and Raman spectroscopy of this oxide product.

GRAPHICAL ABSTRACT



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ABSTRACT

Monophasic Co–Al–CO₃-like layered double hydroxides has been prepared by the coprecipitation method. It has been characterised by Rietveld refinement of the X-ray powder diffraction pattern, DTA-TGA, infrared and Raman spectroscopies. Its structure is trigonal, *R3m* with cell parameters $a = 0.3061(4)$ nm and $c = 2.252(3)$ nm. The decomposition of this hydroxalcite-like structure on heating up to 800 °C yields to a single phase spinel oxide. Besides, infrared and Raman spectroscopies showed the presence of spinel-like domains. The results of Rietveld refinement have revealed that this compound has the *Fd3m* space group ($a = 0.8088(4)$ nm), with crystallographic formula $[\text{Co}_{0.75}\text{Al}_{0.25}]^{\text{8a}}[\text{Co}_{0.252}\text{Co}_{0.77-\text{Al}_{0.98}}]^{16\text{d}}\text{O}_4$, which is of the general formula $\text{Co}_{1.77}\text{Al}_{1.23}\text{O}_4$. This structure is also validated by the charge distribution (CD) analysis.

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Introduction

Layered double hydroxides (LDH), also known as hydroxalcite-like compounds or anionic clays, represent a class of layered materials with chemical composition. They are expressed by the general formula $[\text{M}_{1-x}^{\text{II}}\text{M}_x^{\text{III}}(\text{OH})_2]^{\text{x+}}[\text{X}^{\text{y-}}]_{\text{x/y}}\cdot n\text{H}_2\text{O}]^{\text{x-}}$, symbolized by $[\text{M}^{\text{II}}-\text{M}^{\text{III}}-\text{X}]$, where M^{II} and M^{III} are the divalent and trivalent cations, and $\text{X}^{\text{y-}}$ is an exchangeable interlayer anion.

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Many LDHs have been synthesized with divalent cations such as Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , and trivalent cations such as Al^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} , Ce^{3+} , Y^{3+} and La^{3+} etc. . . [1]. Indeed, the divalent and trivalent metallic cations are randomly distributed in coplanar $\text{M}(\text{OH})_6$ edge-sharing octahedra. They form hydroxylated $\text{M}(\text{OH})_2$ layers similar to those of brucite $\text{Mg}(\text{OH})_2$. The presence of trivalent cations implies that the sheets are positively charged as known in the formula of the pyroaurite. The global electrical neutrality of the compound is obtained by X^- anions distributed between the hydroxylated sheets in disordered interlayer domains, also containing water molecules.

It is possible to intercalate a great variety of simple and complex anions, polyoxometalates, phosphates, phosphonates

and others between the layers to obtain compositionally various and functional materials for use as catalysts [2] and support for catalysts to the intercalation of anionic porphyrins [3–6] or anion exchanges [7]. They are also well-known as the most important precursors for the synthesis of transition metal oxides [8–12] since they have a low decomposition temperature. The decomposition is accompanied with a large mass loss, and an endothermic effect can be observed during heating.

There is an additional interest in the case of Co(II)-based LDH since the product of decomposition is a spinel [8,10,13]. Spinel of Co^{2+} (general formula CoB_2O_4) are technologically important as magnetic storage materials and catalysts. [14–16].

When the LDH of Co with Fe having the formula $[\text{Co}_2\text{Fe}(\text{OH})_6](\text{NO}_3)_n n\text{H}_2\text{O}$ is decomposed, there are several possibilities: (a) the oxide product could be a single phase mixed oxide of the type $\text{Co}^{\text{II}}(\text{Co}^{\text{III}}, \text{Fe}^{\text{III}})\text{O}_4$, or (b) the oxide may segregate into a normal spinel phase, Co_3O_4 and an inverse spinel phase CoFe_2O_4 . What is worthwhile to mention is that the investigation of the Co, Fe spinels system has been undertaken for long by several studies [17–18].

Oxide spinel can be described by the general formula $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{O}_4$, space-group $Fd\bar{3}m$ and $Z=8$. The anionic array is described by the equivalent position 32e, point symmetry 3 m. The A and B cations set in 8a (1/8, 1/8, 1/8), $43m$ (T_d) and 16d (1/2, 1/2, 1/2), $3m$ (D_{3d}), respectively. For example, CoAl_2O_4 normal spinel is presented with this description and with the crystallographic formula $[\text{Co}^{2+}]_8^{\text{a}}[\text{Al}^{3+}]_2^{16\text{d}}[\text{O}^{2-}]_4^{32\text{e}}$. For this structure, the two cationic sites are fully occupied by a single species. On the other hand, in Co_2AlO_4 while the tetrahedral sites are occupied only by Co^{2+} , the octahedral sites are occupied by 8 Co^{3+} and by 8 Al^{3+} with the crystallographic formula: $[\text{Co}^{2+}]_8^{\text{a}}[\text{Co}^{3+}, \text{Al}^{3+}]_2^{16\text{d}}[\text{O}^{2-}]_4^{32\text{e}}$.

Cases of spinel structures, in which two possible octahedral and partially-occupied tetrahedral sites exist, have also been reported [19]. The crystallographic formula is

$([\text{A}\square]_8^{\text{a}}[\text{B}\square]_2^{16\text{d}}[\text{B}'\square]_2^{16\text{c}}[\text{O}_4]_4^{32\text{e}})$, where \square stands for vacancies.

The occupied A, B and B' sites are 8a (1/8, 1/8, 1/8), $43m$ (T_d), 16d (1/2, 1/2, 1/2), $3m$ (D_{3d}) and 16c (0,0,0), $3m$ (D_{3d}), respectively. This is the case, for example, for $\text{Ti}_{0.77}\text{Ni}_{2.44}\text{O}_4$ [13] with the crystallographic formula: $[\text{Ti}_{0.77}^3+\square_{0.33}]_8^{\text{a}}[\text{Ni}^{2+}]_2^{16\text{d}}[\text{Ni}_{0.44}^{2+}\square_{1.56}]_2^{16\text{c}}[\text{O}^{2-}]_4^{32\text{e}}$.

Tomas and Guittard also proposed a new non-stoichiometric spinel $\text{Fe}_{0.76}\text{Yb}_{1.08}\text{S}_4$ [20] with two possible partially-occupied octahedra with the crystallographic formula: $[\text{Fe}^{2+}_{0.76}\square_{0.24}]_8^{\text{a}}[\text{Yb}^{3+}_{0.96}\square_{0.04}]_2^{16\text{d}}[\text{Yb}^{3+}_{0.12}\square_{0.88}]_2^{16\text{c}}[\text{S}^{2-}]_4^{32\text{e}}$.

The present study was undertaken to investigate the Co–Al– CO_3 LDH and their solution decomposition at 800 °C, to deduced if the thermal decomposition of our HDL compound leads to a single phase spinel oxide or a mixture phase of spinel and inverse spinel oxide. We determined the crystallographic formula of product obtained after thermal decomposition and deduced if the metallic cations are distributed in two or three cationic sites. It is based upon the structural refinement using the Rietveld method and characterisations by infrared and Raman spectroscopies.

Experimental

The Co–Al– CO_3 LDHs were prepared by coprecipitation by the pH state method [21]. A solution of 0.1 mol of CoCl_2 and 0.06992 mol of AlCl_3 in 80 ml of distilled water is dropwise added at a constant rate (about 1 ml/min) at room temperature to 100 ml of aqueous solution containing 0.35 mol of NaOH and 0.09 mol of Na_2CO_3 .

The pH was maintained constant (pH = 10) by the dropwise addition of aqueous NaOH (1 mol/l). Once the addition was completed, the solution was maintained at 75 °C for 48 h. The precipitate was filtered, washed several times with distilled water, and then dried at room temperature and at 105 °C for 18 h.

In separate experiments, the dried samples (LDHs) were subsequently calcined under air atmosphere in a muffle furnace with temperature program of 40 °C/h from room temperature to 800 °C. They were followed by a plateau at this temperature for 4 h each to obtain the 800 °C-heated sample (oxide product). This is the temperature from which the cubic structure type spinels are usually obtained [22,23].

X-ray powder diffraction patterns were collected on a Panalytical X'Pert PRO MPD instrument equipped with an X'cellerator detector operating with a secondary monochromator and using a $\text{CuK}\alpha$ radiation source ($K_{\alpha 1} = 1.5406 \text{ \AA}$ and $K_{\alpha 2} = 1.5444 \text{ \AA}$). The diffraction patterns were recorded under ambient atmosphere over a 5–120° (2θ) angular range with 0.02° steps and a counting time of 27.5 s step⁻¹.

The infrared (IR) absorption spectrum was carried out on a pellet sample prepared by mixing 1.0 mg sample for a total weight (samples + KBr) of 200 mg. The spectrum was obtained on a Perkin-Elmer FT-IR system PC spectrophotometer (at the University of Sfax) in the 4000–400 cm^{-1} range (30 scans) with 2 cm^{-1} spectral resolution. A 200 mg KBr pellet was used as reference to correct the background.

The Raman spectra were recorded under microscope using a T-64000 Raman triple monochromator spectrometer (Horiba-Jobin-Yvon). The 514.5 nm wavelength radiation from an Ar/Kr laser was used for the excitation. Typical spectral resolution is 1.5 cm^{-1} .

To estimate the interlayer water content, thermogravimetric (TGA) and differential thermal analysis (DTA). Curve were obtained using a thermal analyzer (SDT Q600 V8.1 Build 99, TA instrument) after equilibrating the sample at room temperature (30 min) and then ramping the temperature up (room temperature up to 800 °C at a rate of 10 °C/min and using 13.66 mg of the sample) in air flow.

Results and discussion

Refinement of the structure

The X-ray diffraction pattern revealed a hydrotalcite-like phase as the main phase (trigonal system, space group $R\bar{3}m$). Profile matching refinements (without atoms) were used to start refinement. Regarding the Rietveld profile refinement method [24], it was used to fit the instrumental parameters for the studied compound using the Fullprof program integrated in WinPLOTR software [25]. Moreover, the zero point, the line asymmetry (three parameters), the two cell parameters and the background were firstly refined (line profile modelled using a pseudo-Voigt function).

A preferential-orientation parameter was refined in the direction of the diffraction vector normal to the layers, it's was derived to correct integrated intensité before structure determination [26]. The profile matching refinement led to the following good agreement factors: $R_B = 6.44\%$ and $R_F = 5.94\%$ with $a = 0.3061(4) \text{ nm}$ and $c = 2.252(3) \text{ nm}$.

The structure of the studied phase was refined as isotypic to the rhombohedral hydrotalcite $[\text{Mg}_{0.64}\text{Al}_{0.36}(\text{OH})_2](\text{CO}_3)_{0.18}, 0.46\text{H}_2\text{O}$ [24].

The structure refinement was initiated by building octahedral coordination for metallic cations. The metals (Co and Al) are distributed in the 3a (0, 0, 0) site of the $R\bar{3}m$ space group.

Accordingly, one constraint, namely $N(\text{Co}) + N(\text{Al}) = 1$ was satisfied, i.e. 3a sites were totally occupied by Co and Al cations.

The oxygen atoms of hydroxyl groups are located in particular positions 6c (0, 0, z). As regards the carbon atoms of the carbonate groups in the interlayer domain species, they are located in 6c (1/3, 2/3, 0.5) positions. Besides, the oxygen atoms of the water molecules and those of the carbonate groups are all located in position 18 h (x, -x, 0.5).

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