



## New acetate-intercalated CoNiFe, ZnNiFe and CoZnFe layered double hydroxides: Synthesis by forced hydrolysis in polyol medium and characterization

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### ABSTRACT

New layered double hydroxides (LDHs) CoNiFe, ZnNiFe and CoZnFe with  $M^{II}/M^{III}$  molar ratio of 3, with acetate ions in the interlayer region have been prepared by forced hydrolysis in polyol medium.

The physico-chemical properties of all products were characterized by the methods of powder X-ray Diffraction, Infrared Spectroscopy, UV-Spectroscopy, Elemental analysis, Thermal analysis, Transmission Electron Microscopy and Scanning Electron Microscopy.

It was found that all compounds present the typical features of hydrotalcite-like structure and exhibit a turbostratic character.

The insertion of acetate anions into LDHs was confirmed and the interlayer spacing values were respectively 12.47, 13.64 and 14.69 Å for CoNiFe, ZnNiFe and CoZnFe.

We notice a difference between the interlayer spacing for all synthesized phases with and without zinc. This can be explained by a structural modification on the level of the layers and/ or different arrangement from the inserted species (anions + water) in the interlayer space for zinc materials.

<sup>57</sup>Fe Mössbauer spectrometry allows concluding the presence of  $Fe^{3+}$  cations which occupy octahedral sites and confirming the absence of  $Fe^{2+}$  in the as-prepared compounds.

### Keywords

Layered Double Hydroxide; Polyol; Forced Hydrolysis; Anionic Exchange; Chemical synthesis; X-ray diffraction; Mössbauer spectrometry

### Academic Discipline And Sub-Disciplines

Solid State Chemistry – Layered Materials

### SUBJECT CLASSIFICATION

Chemistry Subject Classification

### TYPE (METHOD/APPROACH)

Experimental study- synthesis method

# Council for Innovative Research

Peer Review Research Publishing System

**Journal:** Journal of Advances in Chemistry

Vol. 10, No. 9

[editorjaconline@gmail.com](mailto:editorjaconline@gmail.com)

[www.cirjac.com](http://www.cirjac.com)



## 1. INTRODUCTION

Hydrotalcite-like compounds, also called anionic clays or layered double hydroxides (LDHs) are very attractive materials for a broad range of applications [1, 2]. They can be presented by the general formula  $[M^{II}_{1-x}M^{III}_x(OH)_2]^{+x/n}(A^{-n})_{x/n}.mH_2O$ . The positive layer charge is created by substituting a divalent cation with a trivalent one in the octahedral hydroxide layer, with anions ( $A^{-n}$ ) and water in the interlayer space [3].

LDHs are elaborated by several synthesis methods: coprecipitation at fixed pH and exchange reactions [4], reconstruction [5], mechanochemical process [6] and reverse microemulsion method [7]. However the coprecipitation is the most commonly used method with carbonate as the intercalated anion in the most cases. Despite its widespread use, this method presents two main disadvantages. First, it needs a precise control of several parameters mainly the pH. Second, the carbonate anion has a great affinity toward the inorganic layer charged positively. This limits exchange reactions and thus the obtention of LDHs with desired intercalated anions.

Recently an alternative synthesis method has been proposed. It takes advantages from the various properties of polyols. Indeed it has been shown that two main reactions can be easily conducted in such medium: namely reduction and forced hydrolysis along with inorganic polymerization [8] [9]. The competition between these two reactions can be easily controlled by the hydrolysis ratio defined as  $h=nH_2O/nM$ . This led to the synthesis of various inorganic materials: metal, oxides, layered hydroxide salts (LHS) and more recently LDH compounds: LDH-Ni-Al [10] and LDH-Ni-Fe [11] with acetate as the intercalated anion.

In this paper, we want to put this novel route, efficiency for synthesis of a series of layered double hydroxides containing three transition metals CoNiFe, ZnCoFe, and ZnNiFe with acetate anions intercalated in the interlayer space. The obtained LDH are characterised by several complementary analyses (X-ray diffraction, TEM, DTA-TGA, IR, UV and Mossbauer spectroscopy). Such LDHs based on transition metals are of great interest as precursors for metal-spinel oxides composites with potential magnetic and catalytic properties [12].

## 2. EXPERIMENTAL METHODS

### 2.1. Materials

For all preparative procedures,  $Zn(CH_3COO)_2.4H_2O$ ,  $Ni(CH_3COO)_2.4H_2O$ ,  $Fe(CH_3COO)_2$ ,  $Co(CH_3COO)_2.4H_2O$ , NaOH and diethylene glycol (DEG) were purchased from Acros and used without any further purification.

### 2.2. Synthesis of LDHs Samples

The samples were synthesized with a molar ratio (M/Fe) of 3 by forced hydrolysis in polyol medium according to the method described by Poul et al. for elaboration of layered hydroxysalts [8]. It consists in the hydrolysis at 130°C of mixture of acetate salts dissolved in DEG with a total molar concentration of 0.1 mole/L.

The precipitation of the corresponding LDHs occurred when the hydrolysis and alkalinity ratios  $h$  and  $b$  were fixed at 100 and 2 respectively, where  $h=nH_2O/n(M+Fe)$  and  $b=nNaOH/n(M+Fe)$ .

The suspensions were kept under continuous stirring for 6 hours. After separation by centrifugation, the solids CoNiFe-Ac, ZnNiFe and ZnCoFe-Ac were dried under air at 60°C.

### 2.3. Characterization

Powder X-ray diffraction (PXRD) patterns were obtained at room temperature using a Inel diffractometer with Co-K $\alpha$ 1 radiation ( $\lambda_{Co\alpha 1} = 1.7889 \text{ \AA}$ ). The crystallite size was calculated using the Scherrer equation. Scanning electron microscopy study was performed using LEICA STEREOSCAN 440 instrument. Electron microscopy and diffraction studies were performed on a JEOL-100 CX II microscope. Infrared spectra were recorded by transmission on PERKIN ELMER 1750 spectrometer on pressed KBr pellets with  $4\text{cm}^{-1}$  resolution between 400 and  $4000\text{cm}^{-1}$ . Elemental analysis (metal, carbon and hydrogen) was performed by ICP method at the centre national de la recherche scientifique, service central d'analyse à SOLAIZE (France). Differential thermal and thermogravimetric analyses (DTA and TGA) were carried out on a Setaram TG 92-12 thermal analyzer with heating rate  $1^\circ\text{C}/\text{mn}$  under argon, in alumina crucible. UV-Visible spectra were recorded between 200 and 2500 nm, with Cary 5/Varian spectrometer. Polytetrafluoroethylene (PTFE) was used as a reference. The  $^{57}\text{Fe}$  Mössbauer spectra were recorded in a transmission geometry using a  $^{57}\text{Co}/\text{Rh}$   $\gamma$ -ray source. They were analyzed by a least-squares fitting method to lorentzian function. The isomer shifts ( $\delta$ ) were referred to that of  $\alpha$ -Fe at 300 K. The sample (area:  $3\text{ cm}^2$ ) has been prepared by dispersion of the compound (40 mg) in a specific resin.

## 3. RESULTS AND DISCUSSION

### 3.1. X-ray diffraction study

The X-ray diffraction patterns of all the synthesized compounds (**Fig. 1**) have typical features of turbostratic lamellar compounds [13]. Indeed, three (00 $l$ ) sharp and symmetric peaks at low diffraction angles, and two broad, less intense and asymmetric peaks can be clearly identified. The patterns were indexed in a hexagonal lattice with rhombohedral symmetry (R-3m), commonly used as a description of the layered double hydroxide structure [14]. The value of the crystallographic parameter  $a$  which is the average metal-metal distance in the brucite-like layers of the LDH compounds, has been

calculated from  $d_{110}$  ( $a=2d_{110}$ ), whilst, the value of parameter  $c$  which is related to the thickness of the brucite-like layers, the nature of the interlayer anion and water content, has been also determined.

The insertion of acetate anions into LDHs was confirmed and the interlayer spacing values were respectively 12.47, 13.64 and 14.69 Å for CoNiFe, ZnNiFe and ZnCoFe (Table 1).

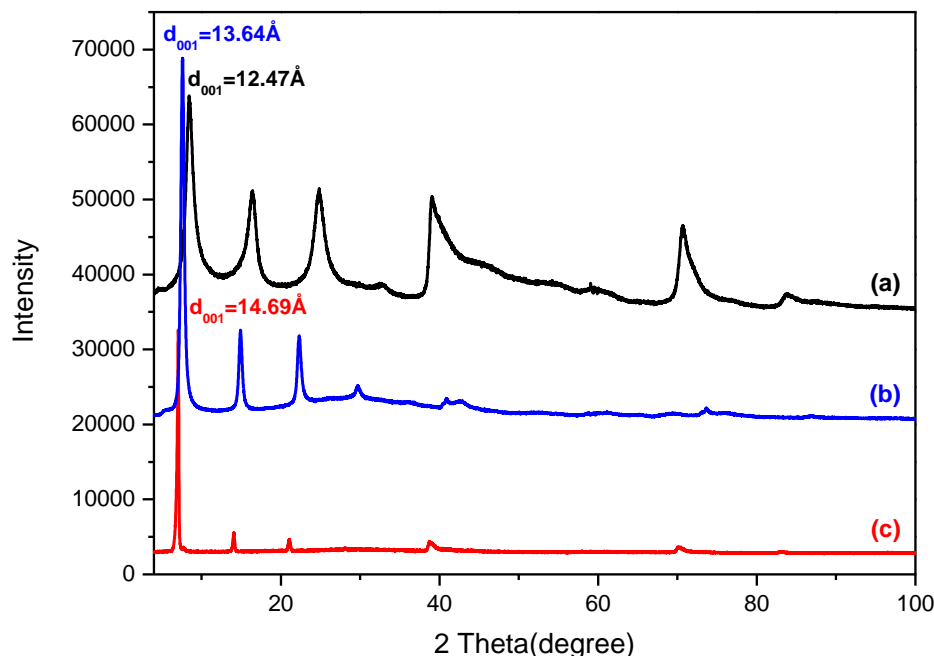


Figure 1: XRD patterns of LDHs, (a) CoNiFe-Ac, (b) ZnNiFe-Ac, (c) ZnCoFe-Ac.

Table 1: Lattice parameters (from XRD data) of LDH samples

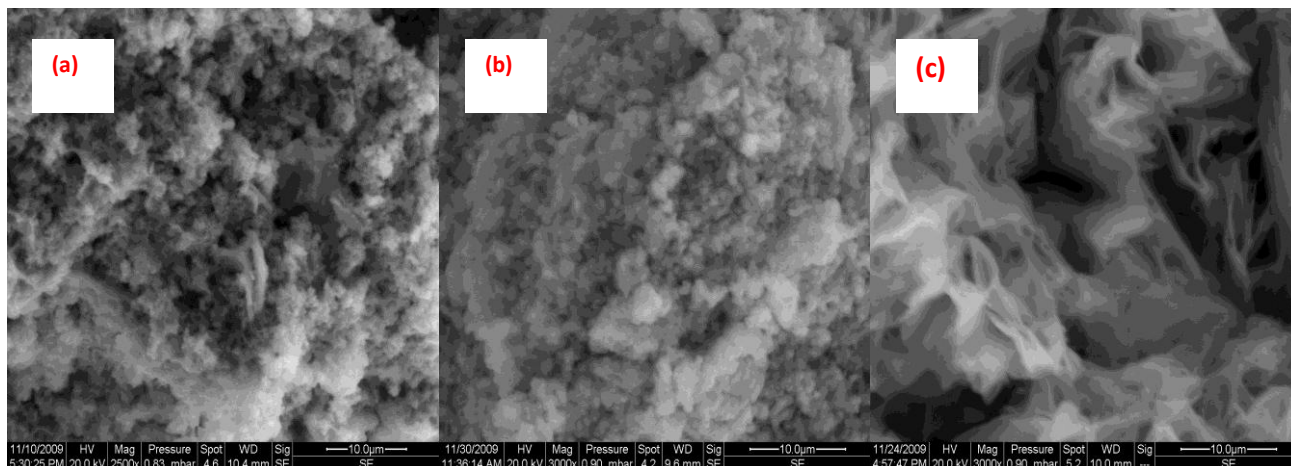
Compound	$a=2d_{110}$ (Å)	$d_{001}$ (Å)	Correlation length according to $c$ axis (Å)	Number of monolayers /crystallite
CoNiFe-Ac	3.08	12.47	60	5
ZnNiFe-Ac	3.06	13.64	228	16
ZnCoFe-Ac	3.10	14.69	490	33

We notice a difference between the interlayer spacing for all synthesized phases. This can be explained by a structural modification on the level of the layers and/ or different arrangement for the inserted species (anions + water) in the interlayer space for zinc materials. The correlation length along  $c$  deduced from the XRD analysis (Table 1) reveals a better crystallinity for ZnCoFe-Ac in comparison with CoNiFe-Ac and ZnNiFe-Ac compounds. In this case, it corresponds to the stacking of approximately 33 layers by crystallite.

### 3. 2. Morphology

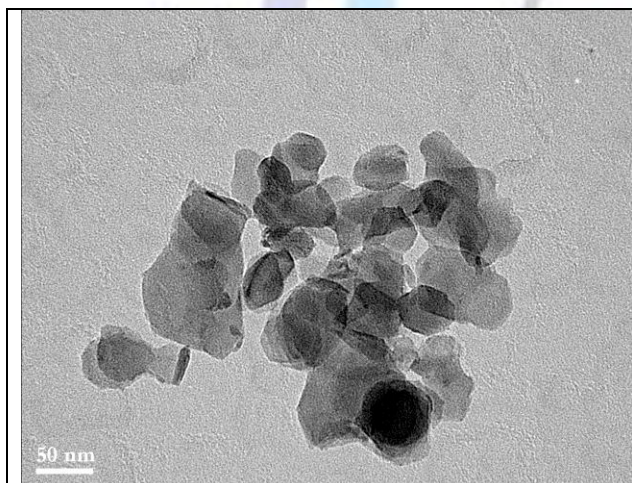
SEM images of all synthesized materials show the low level of crystallinity and confirm the turbostratic character of these compounds. Fig. 2(a) and (b) depict the SEM images of CoNiFe-Ac and ZnNiFe-Ac systems respectively, it is clearly seen that these particles are precipitated as small, pseudo-spherical aggregates of platelets; they are also very similar to the morphology of other LDHs [15].

The particles of ZnCoFe-Ac (Fig. 2(c)) sample are formed by the aggregation of small platy crystallites without any definite shape. They appear to be denser compared to those of the CoNiFe-Ac and ZnNiFe-Ac.

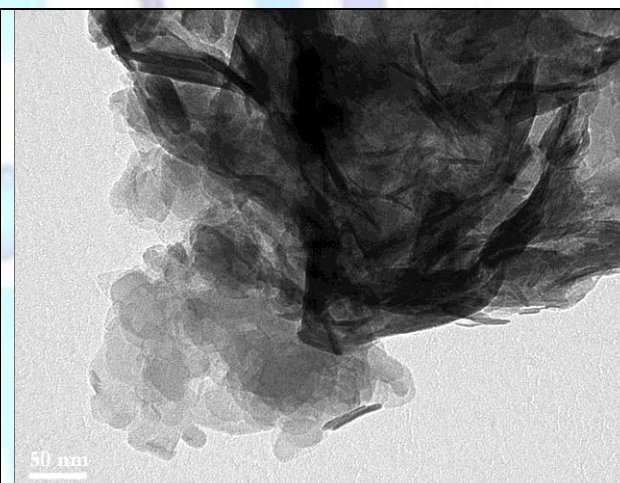


**Figure 2: SEM images of LDHs, (a) CoNiFe-Ac, (b) ZnNiFe-Ac, (c) ZnCoFe-Ac.**

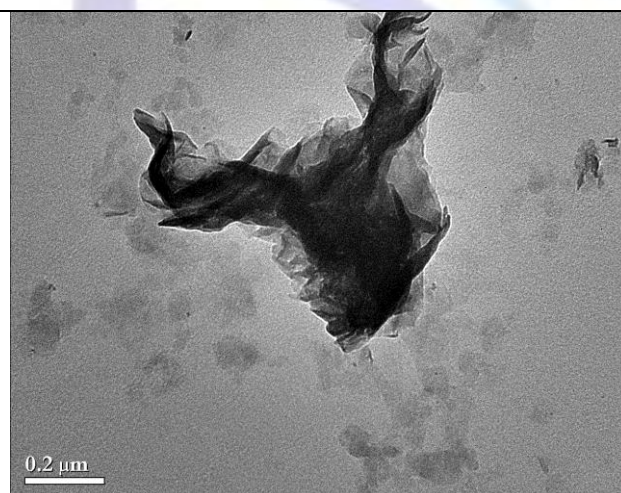
For TEM images, the particles of all compounds appear as aggregates of thin crumpled sheets with irregular size and shape (**Fig. 3**). This aggregation is similar to that described by Taibi et al. for NiFe-Ac LDH [11]. Electron diffraction pattern of these samples confirm the hexagonal symmetry of the brucite structure, to which all the hydroxalcite-like materials belong. The preferential orientation of the crystallites along the (00) hexagonal plane is clearly established for CoNiFe sample (**Fig. 4**).



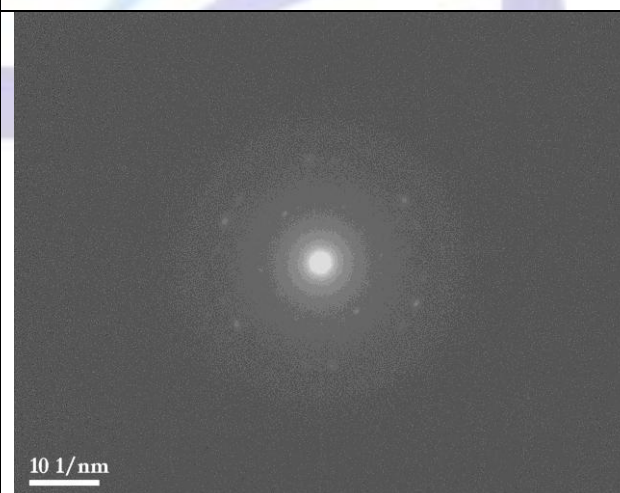
**Figure 3: TEM images of LDHs CoNiFe-Ac.**



**Figure 3: TEM images of LDHs ZnNiFe-Ac.**



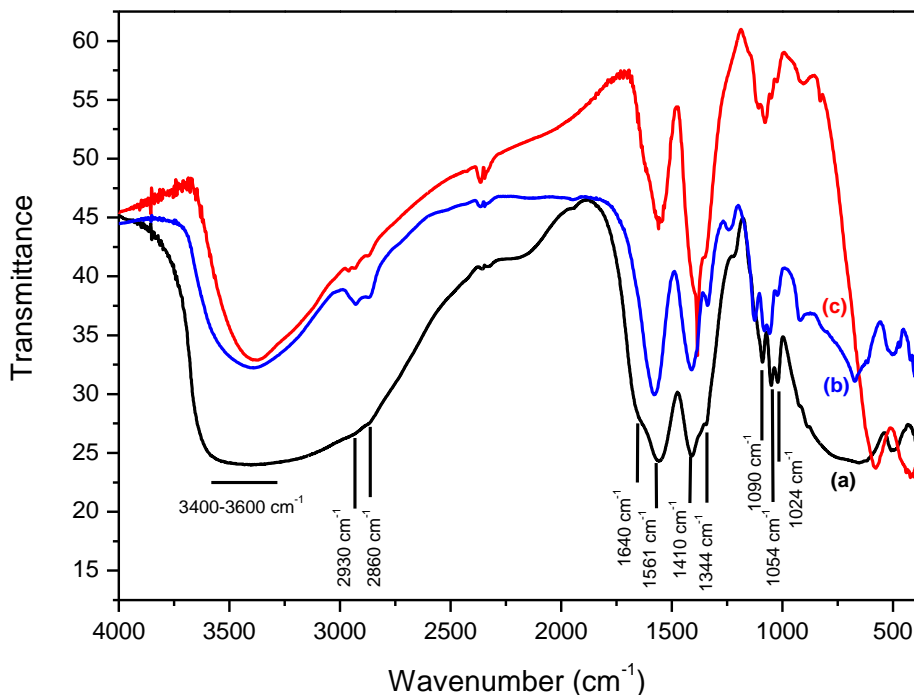
**Figure 3: TEM images of LDHs ZnCoFe-Ac.**



**Figure 4: Electronic diffraction of LDHs CoNiFe-Ac.**

### 3. 3. Infrared Spectroscopy

IR spectra for all samples are shown in **Figure 5**. The broad absorption bands at high frequency ( $3600\text{-}3400\text{ cm}^{-1}$ ) indicate the presence of OH groups and water molecules in the brucite-like layer. The absorption band around  $1640\text{ cm}^{-1}$  for CoNiFe-Ac and ZnCoFe-Ac is assigned to  $\delta\text{H}_2\text{O}$  vibration of the water molecules [16, 17]. In the case of ZnNiFe-Ac, this band is obscured by the strong band due to the  $\nu_{\text{as}}(-\text{COO}^-)$  of the acetate anion [18].



**Figure 5:** FT-IR spectra LDHs (a) CoNiFe-Ac, (b) ZnNiFe-Ac, (c) ZnCoFe-Ac.

The presence of acetate anions in the interlayer of all compounds is attested by the presence of two large and intense bands in  $1600\text{-}1000\text{ cm}^{-1}$  domain, which are assigned to  $\nu_{\text{as}}(-\text{COO}^-)$  and  $\nu_{\text{s}}(-\text{COO}^-)$  respectively.  $\nu_{\text{as}}(-\text{COO}^-) = 1561\text{ cm}^{-1}$  for CoNiFe-Ac and ZnCoFe-Ac and  $1579\text{ cm}^{-1}$  for ZnNiFe-Ac.  $\nu_{\text{s}}(-\text{COO}^-) = 1410\text{ cm}^{-1}$  for CoNiFe-Ac and ZnNiFe-Ac and  $1386\text{ cm}^{-1}$  for ZnCoFe-Ac [19].

According to Nakamoto rules [20], the value of  $\Delta\nu = (\nu_{\text{as}} - \nu_{\text{s}})$ , where  $175 \leq \Delta\nu \leq 151\text{ cm}^{-1}$  confirms that acetate anions are intercalated as free species in between the layers.

The absorption bands around  $1344\text{ cm}^{-1}$  are attributed to  $\text{CH}_3$  vibrations [19]. The existence of a low-intensity bands between  $1300$  and  $1000\text{ cm}^{-1}$  indicate the presence of DEG molecules as adsorbed species [11]. Bands at lower wavenumber ( $\nu < 800\text{ cm}^{-1}$ ) are due to vibrations implying M-O, M-O-M and O-M-O bonds in the layer [17, 21].

The band close to  $1360\text{ cm}^{-1}$  is absent in all spectra, confirming the intercalation of all compounds with acetate anions without any trace impurity of carbonate anions.

### 3. 4. Thermal analysis

The TG/DTA analysis for all samples is shown in **Figure 6**. Three weight losses are observed for each sample. The first weight loss corresponds to the removal of adsorbed and interlayer water molecules, the second weight loss is due to dehydroxylation of the brucite-like layers, while the third one is due to the removal of interlayer anions [22].

For all compounds, three endothermic effects can be distinguished in the DTA curve. The first endothermic peak due to the loss of surface and interlayer water was observed at  $116^\circ\text{C}$  with loss of mass of 6.3% for CoNiFe-Ac, at  $83^\circ\text{C}$  (7.3%) for ZnNiFe-Ac and at  $82$  and  $127^\circ\text{C}$  (9.4%) for ZnCoFe-Ac.

The second effect, attributed to the dehydroxylation process, was seen at  $187^\circ\text{C}$  (10.3%) for CoNiFe-Ac, at  $132$  and  $229^\circ\text{C}$  (13%) for ZnNiFe-Ac and at  $200^\circ\text{C}$  (10.3%) for ZnCoFe-Ac.

The third and the last endothermic effects which are likely related to the decomposition of acetate anions, appeared at  $290^\circ\text{C}$  and  $430^\circ\text{C}$  (29.3%) for CoNiFe-Ac, at  $288$  and  $414^\circ\text{C}$  (31%) for ZnNiFe-Ac and at  $292^\circ\text{C}$  (21.4%) for ZnCoFe-Ac.

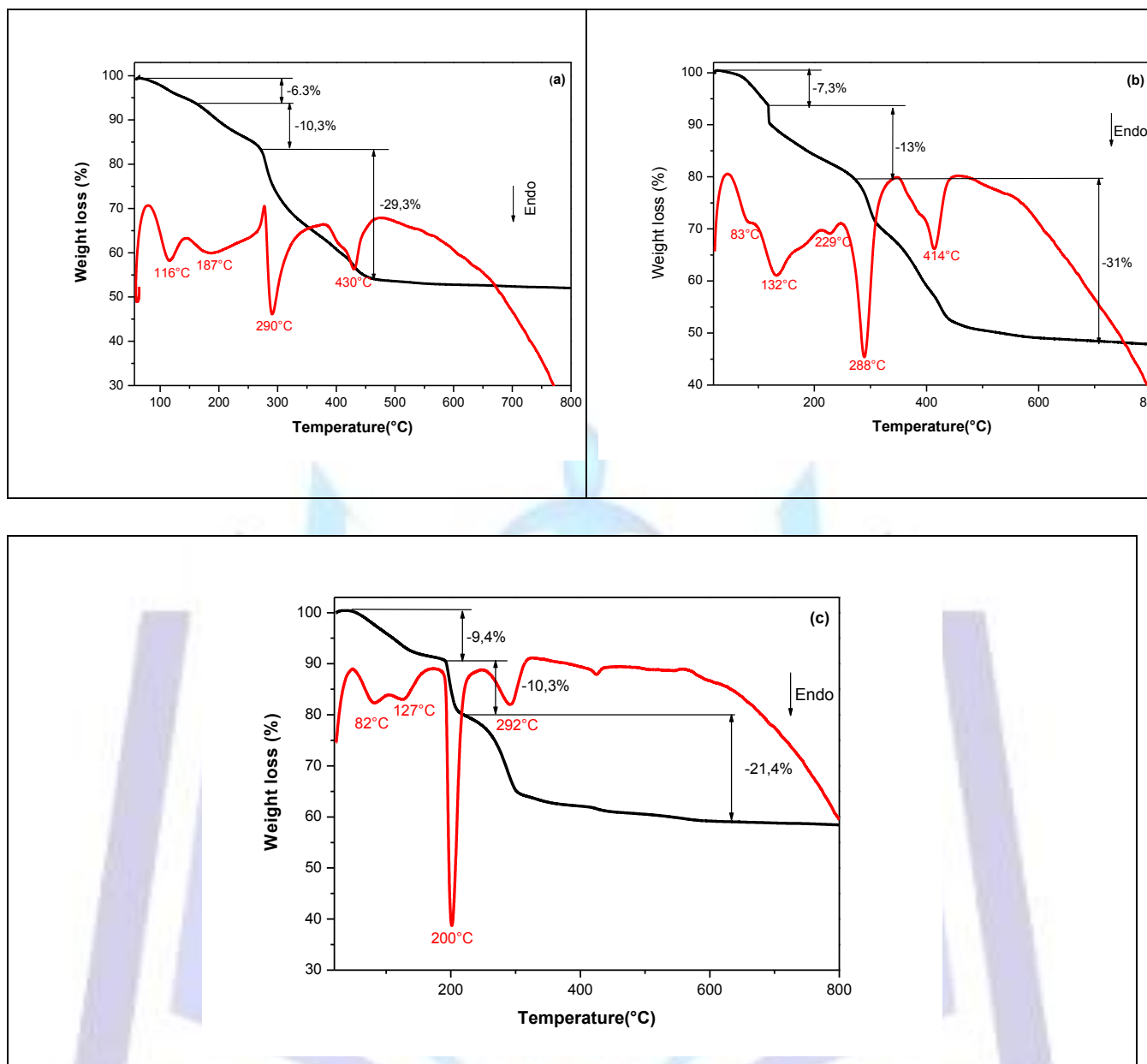


Figure 6: TG/DTA curves of LDHs (a) CoNiFe-Ac, (b) ZnNiFe-Ac, (c) ZnCoFe-Ac.

### 3. 5. Chemical analysis

First it should be noted that under synthesis conditions,  $\text{Fe}^{2+}$  was oxidized to  $\text{Fe}^{3+}$  as confirmed by Mössbauer analysis (as shown hereafter). This is due to the presence of a sufficient amount of water able to oxidize ferrous ion. In **Table 2**, are summarized the results of elemental chemical analysis of the compounds and their corresponding formulae. It can be observed that in CoNiFe-Ac compound, the calculated  $\text{M}^{\text{II}}/\text{Fe}^{\text{III}}$  ratio is in a good agreement with the experiment data, but in ZnNiFe-Ac and ZnCoFe-Ac this ratio is larger than in the starting solution.

For all samples, the results show that the observed carbon amount is higher than that expected in the acetate anions; this is due to the adsorption of polyol (DEG) on the surface of compounds as has been seen in the IR study.

Similar results have been observed for Ni-Co hydroxyacetates prepared in polyol medium [23], where the amount of adsorbed polyol has not been taken into account in the chemical formula.



**Table 2: Elemental chemical analysis data of LDH samples**

Compound	Mass fractions (%)						Molar ratio M <sup>II</sup> /Fe <sup>III</sup>		X=M <sup>III</sup> /M <sup>II</sup> +Fe <sup>III</sup>	
	Co	Ni	Zn	Fe	C	H	solution	solid	solution	solid
CoNiFe-Ac	17.32	17.33		10.36	6.88	3.61	3	3.17	0.25	0.24
ZnNiFe-Ac	-	22.05	12.99	8.27	6.35	3.18	3	3.87	0.25	0.20
ZnCoFe-Ac	24.59	-	22.46	10.1	7.79	3.61	3	4.24	0.25	0.19
Compound	Chemical formula						DEG	H <sub>2</sub> O %	Total weight loss (%)	
									Exp	Exp
CoNiFe-Ac	Co <sub>0.38</sub> Ni <sub>0.38</sub> Fe <sub>0.24</sub> (OH) <sub>2</sub> Ac <sub>0.24</sub> , 0.52H <sub>2</sub> O						0.090	06.3	45.9	47.8
ZnNiFe-Ac	Zn <sub>0.28</sub> Ni <sub>0.52</sub> Fe <sub>0.20</sub> (OH) <sub>2</sub> Ac <sub>0.20</sub> , 0.70H <sub>2</sub> O						0.097	07.3	51.3	50.3
ZnCoFe-Ac	Zn <sub>0.37</sub> Co <sub>0.44</sub> Fe <sub>0.19</sub> (OH) <sub>2</sub> Ac <sub>0.19</sub> , 0.18H <sub>2</sub> O						0.044	09.4	41.7	41.1

In our study, the amount of adsorbed polyol in the final products has been included in the chemical formula to calculate the theoretical weight losses, which are consistent with those observed by TGA analysis (Table 2). Altogether, these results led to the chemical formula M<sup>2+</sup><sub>1-x</sub> Fe<sup>3+</sup><sub>x</sub> (OH)<sub>2</sub> (CH<sub>3</sub>COO)<sub>x</sub> .mH<sub>2</sub>O.nDEG (see Table 2 for exact formula).

### 3. 6. UV-Visible Spectroscopy

For CoNiFe-Ac and ZnCoFe-Ac, the absorption bands at around 1200 and 500 nm (Fig. 7(a) and (c)) are attributed to the d-d transitions of octahedral coordinated Co<sup>2+</sup> [24]. They are assigned as v<sub>1</sub>(Co<sup>2+</sup>):<sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(F), v<sub>2</sub>(Co<sup>2+</sup>):<sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>A<sub>2g</sub>(F), and v<sub>3</sub>(Co<sup>2+</sup>):<sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P) transitions in high spin state Co<sup>2+</sup> (d<sup>7</sup>) respectively [23,25, 26]. The UV-Visible spectra of the CoNiFe-Ac and ZnNiFe-Ac (Fig. 7(a) and (b)) show that Ni<sup>2+</sup> ions are also located in octahedral sites with the presence of absorption bands at around 380, 665 and 1115 nm due to v<sub>2</sub>(Ni<sup>2+</sup>):

<sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F), v<sub>3</sub>(Ni<sup>2+</sup>): 3A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P), and v<sub>1</sub>(Ni<sup>2+</sup>): 3A<sub>2g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F) respectively [27-31]

(Table 3).

**Table 3: UV-Visible bands attribution of LDH samples**

Samples	Co <sup>2+</sup> (Oh)			Ni <sup>2+</sup> (Oh)		
	v <sub>1</sub> ( <sup>4</sup> T <sub>2g</sub> (F)),	v <sub>2</sub> ( <sup>4</sup> A <sub>2g</sub> (F)),	v <sub>3</sub> ( <sup>4</sup> T <sub>1g</sub> (P))	v <sub>1</sub> ( <sup>3</sup> T <sub>2g</sub> (F)),	v <sub>2</sub> ( <sup>3</sup> T <sub>1g</sub> (F)),	v <sub>3</sub> ( <sup>3</sup> T <sub>1g</sub> (P))
	/nm	/nm	/nm	/nm	/nm	/nm
CoNiFe-Ac	1200	625	550	1402	752	380
ZnNiFe-Ac	-	-	-	1115	665, 572	380
ZnCoFe-Ac	1220	625	550	-	-	-

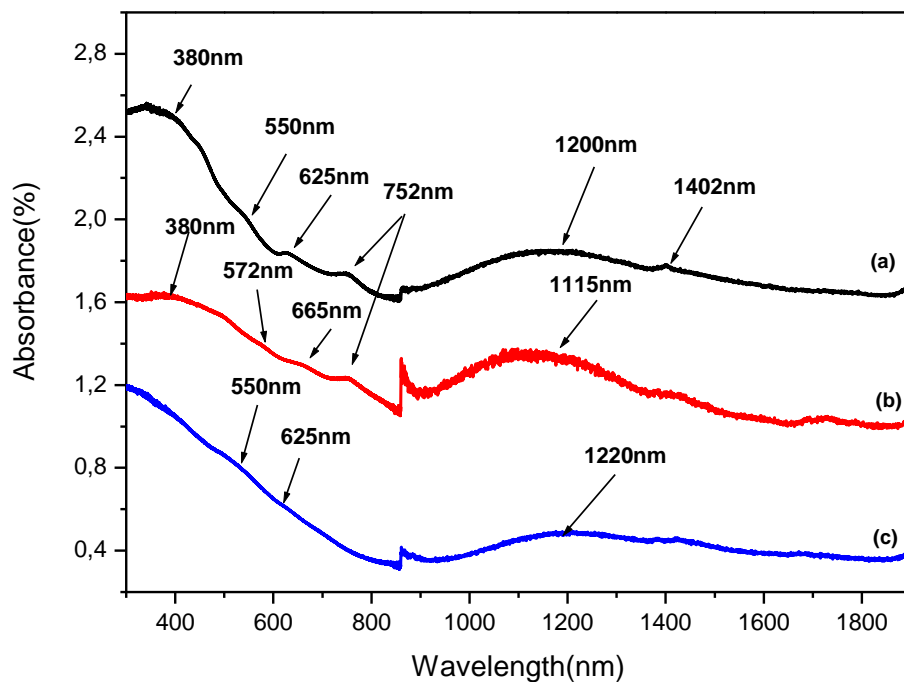


Figure 7: UV-Visible of LDHs (a) CoNiFe-Ac, (b) ZnNiFe-Ac, (c) ZnCoFe-Ac.

### 3. 7. Mössbauer Spectroscopy

Fig.8 shows the Mössbauer spectra for all samples at room temperature in order to probe local magnetic environment around the Fe sites and to determine the oxidation state of the Fe in LDHs matrix.

Each spectrum shows only one doublet with isomer shift ( $\delta$ ) ranging from 0.33 to 0.34 mm/s and quadrupole splitting ( $\Delta$ ) 0.45 - 0.56 mm/s indicating  $\text{Fe}^{3+}$  nature of the Fe atom, and no evidence of  $\text{Fe}^{2+}$  signal was found [32]. The small value of quadrupole splitting ( $\Delta$ ) corresponds to high spin  $\text{Fe}^{3+}$  ions in octahedral site.

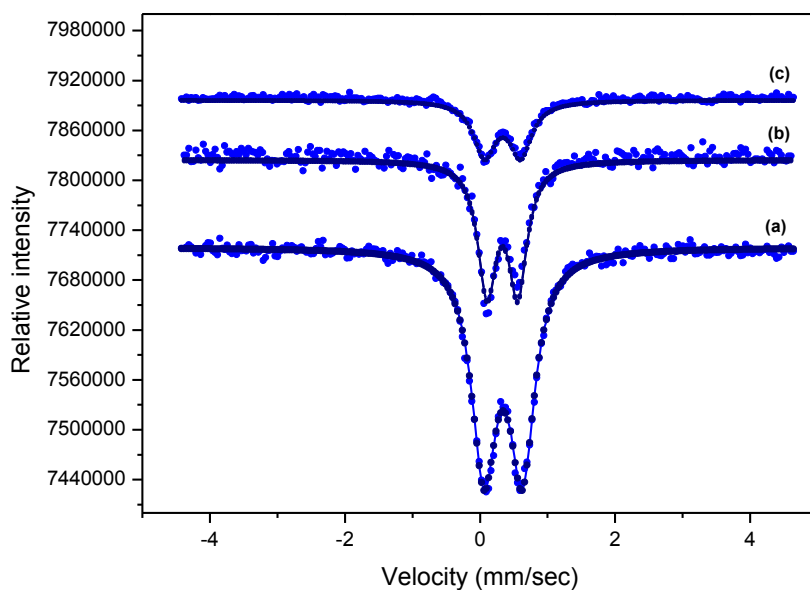


Figure 8: Mössbauer spectra of LDHs (a) CoNiFe-Ac, (b) ZnNiFe-Ac, (c) ZnCoFe-Ac.





## 4. CONCLUSION

In the current study, a novel series of ternary layered double hydroxides with acetate anion intercalated in the interlayer region has been prepared by forced hydrolysis in polyol medium, in the ratio range  $3.17 \leq M^{II}Fe^{III} \leq 4.24$ .

X-Ray diffraction investigations show that these materials derive from the brucite structure with variable basal spacing, the Zinc based compounds having the more higher interlamellar distances.

IR study shows that acetate anions are located in between the brucite sheets as free species. No trace of carbonate  $CO_3$  anion was detected.

Because of the turbostratic character of CoNiFe-Ac, ZnNiFe-Ac and ZnCoFe-Ac, it was hard to get more insight into their intralayer structural organization by X-ray diffraction analysis. Thus two complementary analysis techniques namely UV-Visible and Mössbauer Spectroscopy have been used.

For all samples, UV-Visible spectra present characteristic bands of  $Co^{2+}$  and  $Ni^{2+}$  in octahedral sites, and  $^{57}Fe$  Mössbauer measurement reveals that Fe atoms are present in the LDHs lattice in  $Fe^{3+}$  state and no such  $Fe^{2+}$  ions are present.

Owing to their chemical compositions, these based 3 d-transition LDHs are believed to be very versatile precursors for a wide range of metal-spinel nanocomposites.

## ACKNOWLEDGMENTS

Mossbauer measurements have been conducted at the LPEC – UMR / CNRS 6087 – Université du Maine – Le Mans – France. We are grateful to Dr. Jean-Marc Grénèche for this collaboration.

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