BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 69 (73), Numărul 1, 2023
Secţia
CHIMIE și INGINERIE CHIMICĂ
DOI: 10.5281/zenodo.7766972

USING XRD AND TG/DTG/DSC STUDIES TO FOLLOW THE STRUCTURAL CHANGES INDUCED BY THE SUBSTITUTION OF Al^{3+} WITH Ga^{3+} IN 2-D Zn-RICH LAYERED DOUBLE HYDROXIDES MATRICES

BY

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Received: November 20, 2022
Accepted for publication: January 10, 2023

Abstract. Changes in the structural characteristics of ZnAlLDHs, when Al^{3+} was replaced by Ga^{3+} and the structural features of the mixed oxide derived by calcination were rigorously assessed using X-ray diffraction (XRD) and thermogravimetric analysis (TG/DTG/DSC). The results of XRD analysis point out the formation of an LDH phase, without any impurity, with slight differences between samples prepared with specific trivalent cations, in relation to the higher volume of Ga compared to Al, due to their different cationic rays. After the calcination, the LDH structure collapsed and the characteristic XRD reflections of the mixed oxides were obtained. The results of the TG/DTG/DSC analysis indicate that the mass loss reported in terms of moles was almost similar for ZnAlLDH and ZnGaLDH. This demonstrates that the adsorbed water, CO_2 and HO^- content are similar in the substituted LDH. Hence, this study has revealed that both the composition of the Zn-rich LDHs and the calcination temperature are important parameters for tailoring the structural characteristics of the newly formed $ZnO/Ga_2O_3/ZnGa_2O_4$ homogeneous mixed oxides.

Keywords: Layered double hydroxides, mixed oxides, X-Ray diffraction, thermogravimetric analysis, structural properties.

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1. Introduction

LDHs are represented by general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}\cdot A^{n-}_{x/n}\cdot mH_2O$, where Me^{II} and Me^{III} are cations in the layers (e.g., Mg^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+}, Al^{3+}, etc.) and A^{n-} are interlayer anions; coefficient *x* represents the cation molar ratio (Carja *et al*., 2018).

Thermal treatment of LDH leads to a collapse in the LDH 2D layered structure and continuously the MMOs formation which are self-possessed of metal oxide and spinel phases. Recently, MMOs have shown great interest among research society as supercapacitor, anode materials in lithium-ion batteries, and photo-catalyst especially in the visible light region, due their unique mesoporous nature (Salih *et al*., 2021).

In recent years, researchers have described two-dimensional (2D) inorganic nanomaterials as strong points in the fields of nanotechnology, with wide applications in current fields (biomedicine, photocatalysis, electrochemistry, etc.) due to their specific properties. In order to improve the catalytic and electrochemical properties of layered double hydroxides (LDH), it is necessary to replace them with different metals.

In this study, we report the investigation of the change in the structural properties of ZnAlLDH and ZnGaLDH following their thermal decomposition by calcination at 750°C and 925°C as a result of the formation of mixed metal oxides (MMO) composed of metal oxide and spinel phases. LDHs containing zinc and Al/Ga in the layers with a cation ratio of 3/1 were synthesized by the co-precipitation method at constant pH. Changes in the structural characteristics of ZnMeLDHs when aluminium was replaced by gallium and of mixed oxide derivatives were investigated using X-ray diffraction (XRD) and thermogravimetric analysis (TG/DTG). After the calcination, the LDH structure collapsed and the characteristic XRD reflections of the mixed oxides were obtained. The XRD results disclosed the formation of $ZnO/ZnAl_2O_4/ZnGa_2O_4$ and $ZnO/Ga_2O_3/ZnGa_2O_4$ nanoscale assemblies derived from ZnMe (Me = Al/Ga). The results of the thermal analysis show that the loss of mass recounted in terms of moles was almost the same for ZnAlLDH and ZnGaLDH.

2. Experimental

2.1. Materials Preparation

The LDHs containing zinc and Al/Ga in the layers with a cation ratio of 3/1 were synthesized following by the co-precipitation method at a constant pH. In a specific synthesis method, combined solutions of zinc nitrates ($Zn(NO_3)_2\cdot 6H_2O$) / gallium nitrate ($Ga(NO_3)_3\cdot 18H_2O$) and zinc nitrates ($Zn(NO_3)_2\cdot 6H_2O$) / aluminium nitrates (($Al(NO_3)_3\cdot 9H_2O$), respectively, with Zn^{2+}/Me^{3+} molar ratios of 3/1, were added slowly, under vigorous stirring, to a

beaker together with the precipitants solutions Na_2CO_3/NaOH. By rigorously controlling the flow rate of the solutions of precursors salts and precipitating agents, a constant pH value of 8.5 was ensured. The resulting sample was then matured for approximately 24 hours under gentle agitation at room temperature, then recovered by filtration, washed with bidistilled water three times and dried at 80°C for 12 h. The samples were denoted as ZnGaLDH and ZnAlLDH. The samples calcined at 750°C and 925°C for 5 hours were denoted as ZnGaLDH_750, ZnGaLDH_925 and ZnAlLDH-950 ZnAlLDH_750, respectively).

2.2. Materials Characterization

The structural analysis of the samples was carried out by powder X-ray diffraction (XRD) using a diffractometer XPERT-PRO by monochromatic light CuKα radiation (α = 1.54060 Å), operating at 45 kV and 40 mA, 2θ range 5.0084 - 79.9784°, step size 0.0170°. Rhombohedral symmetry 3R was present in LDHs. To find out the structural parameters, the calculation relations were used: a = 2 d[110] and c = 3 d[003], where the indexes indicate the orientations of these two characteristic planes. The investigation of the thermal stability of the samples up to the temperature of 900°C was carried out by using an equipment Perkin Elmer equipment consisting of a TG/DTG/DSC Diamond thermo-balance.

3. Results and Discussions

At the structural level, the most important characterization technique is X-ray diffraction, a technique that provides information on the degree of crystallinity, the existing phases in the material, the type of network, etc.

In Fig. 1 we present the XRD pattern of the synthesized ZnAlLDH prior to calcination which looks like were obtained three pronounced peaks: (003), (006), and (009) as confirms the attainment of LDH structure. was perceived an additional peak at 2θ = 34°, which can be indexed to the existence of ZnO phase (Salih *et al.*, 2022).

Further Fig. 1 shows the XRD pattern of ZnAlLDH_750 through which the diminishment of LDH structure had occurred. Was observed subsequent to the calcination process of LDH trinary crystal growth.

On the other hand, the XRD of ZnO–$ZnAl_2O_4$ (see Fig. 1), obtained after calcination at 750°C, demonstrated the presence of reflection peaks corresponding to both ZnO and $ZnAl_2O_4$.

The reflection peaks for $ZnAl_2O_4$ are clearly observed at 2θ = 31.4; 36.85; 44.83; 49.3; 55.7; 59.42 and 65.5, corresponding to reflection planes (220), (311), (400), (331), (422), (511) and (440), respectively, while those of ZnO are observed at 2θ = 34.6; 36.3; 47.8; 56.6; 62.8; 66.4; 68 and 69.4, corresponding to

reflections planes (100), (002), (101), (102), (110), (103), (200), (112) and (201), respectively. These results are in agreement with previously reported data (Gilea *et al.*, 2017). The newly emerging XRD patterns indicated the total destruction of ZnAl–LDH double lamellar structure to form the desired ZnO–$ZnAl_2O_4$ product. (Ghribi *et al*., 2020). This indicates that Al^{3+} did not result in structural changes in the MMO matrix. Also, there is no appearance of Al and/or Al oxide, which confirms that ions of Al^{3+} substituted Zn^{2+} ions within the MMO matrix (Salih *et al*., 2022).

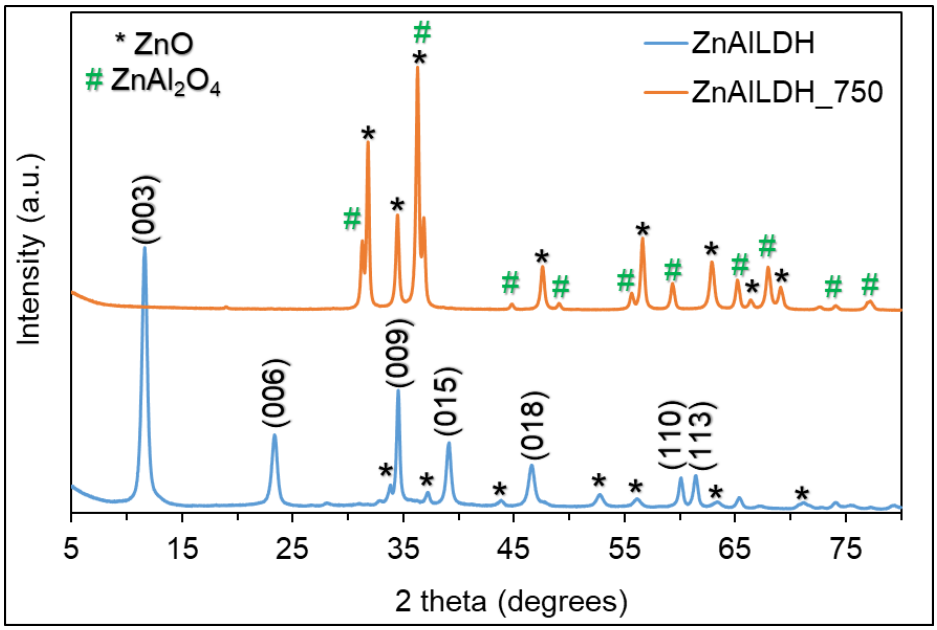

Fig. 1 − XRD spectra of ZnAlLDH and ZnAlLDH_750.

Figure 2 reports the XRD patterns of ZnGaLDH prior to calcination, those patterns reflected the presence of a hydrotalcite-like LDH structure, without any impurity. We also observed a series of (00l) reflection peaks, sharp, symmetric and basal, at low 2θ range, namely (003), (006) and (009) and broad, asymmetric, less relieved peaks, attributed to non-basal planes (015) and (018) planes. The reflections corresponding to the plans [110] and [113] are found at higher values to the angle 2θ (60 degrees). After calcination at 750°C and 925°C, the collapse of the LDHs structure has occurred, obtaining the difractograms characteristic of mixed oxides.

After the calcination at 750°C and 925°C, the sample ZnGaLDH suffers progressively deeper structural transformations, forming highly crystalline mixed

oxides (Fig. 2). Thermal treatment of ZnGaLDH over a wide temperature range led to the formation of mixed oxides illustrated as $ZnO/Ga_2O_3/ZnGa_2O_4$.

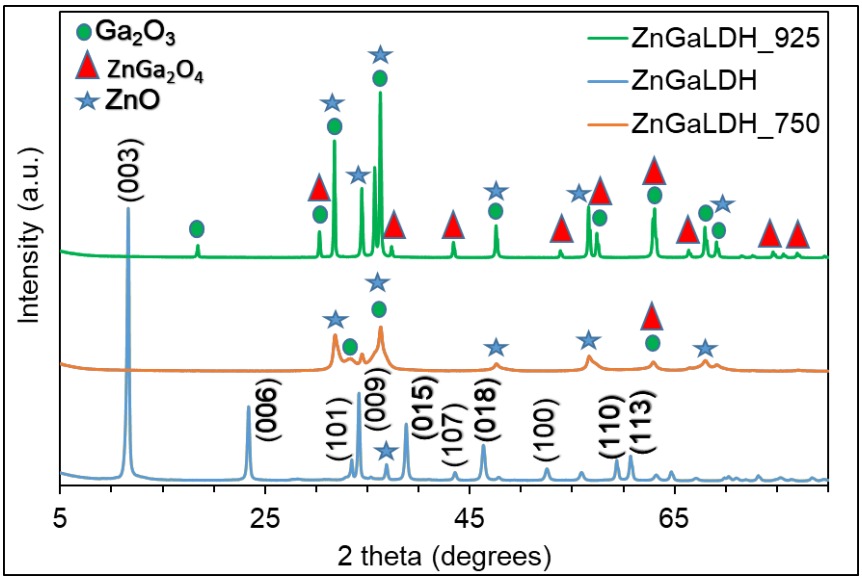

Fig. 2 − XRD spectra of ZnGaLDH and ZnGaLDH_750, ZnGaLDH_925.

The reflection peaks for $ZnGa_2O_4$ are clearly observed at $2\theta = 30.6$; 37.8; 43.3; 54.5; 57.6 and 63 corresponding to reflection planes (220), (222); (400); (422), (511) and (440), respectively. The reflection peaks for β-Ga_2O_3 are observed at $2\theta = 18.5$; 30.2; 35.5; 47.9; 57.5 and 62.8 corresponding to reflection planes (020); (400); (111); (511); (313) and (-710) respectively, while those of ZnO are observed at 32; 34.5; 36.5; 47.6; 56.9 and 69.3 corresponding to reflection planes (100); (002); (101); (102); (110) and (201).

Were successfully calculated the lattice parameters a and c from the latter reflection planes including the (110) plane, with $a = 2d_{110}$ and $c = 3d_{003}$ (Table 1).

Table 1

Structural parameters of the investigated samples

Sample	d_{003} (Å)	2Θ (º)	d_{110} (Å)	2Θ (º)	c (Å)	a (Å)	IFS
ZnAlLDH	7.628	11.5908	1.5398	60.0338	22.885	3.079	2.828
ZnGaLDH	7.612	11.6158	1.556	59.3208	22.836	3.113	2.812

The average crystallite size in the c direction has been calculated used the Scherrer equation (Eq. (1)) (Ghribi *et al*., 2020) (Table 2).

$$d_{hkl} = \frac{k\,\lambda}{\beta\,cos\theta} \quad (1)$$

where λ is the X-ray wavelength, θ is the Bragg's diffraction angle and β is the full-width at half-maximum in radian.

Interlamellar free space was calculated with the formula:

$$IFS = d_{003} - 4.8\ Å \quad (2)$$

According to the Table 1, the value of the parameter a is higher for ZnGaLDH compared to ZnAlLDH, which is explained by the higher ionic radius of Ga^{3+} (0.62 Å) than that of Al^{3+} (0.53 Å) (Grosu *et al*., 2022).

The values obtained for d_{003} (~0.76 nm) in both samples, show the presence of interlayers anion CO_3^{2-}in the LDHtype catalysts (Grosu *et al*., 2022).

Table 2

Crystallographic data on precursor anionic clays

Sample	Crystallite size (nm)						
	(003)	(006)	(009)	(015)	(018)	(110)	(113)
ZnAlLDH	15.917	16.295	31.384	23.878	16.204	28.129	27.025
ZnGaLDH	34.794	36.896	51.185	37.730	31.341	41.853	40.763

Using the equation Scherrer, the crystallite size was calculated for ZnO if calcined materials and the results are showed in Table 3.

Table 3

Crystallite size of the ZnO if ZnAlLDH and ZnGaLDH calcined materials

Sample	Crystallite size (nm)					
	(100)	(002)	(101)	(102)	(110)	(201)
ZnAlLDH_750	38.056	27.658	30.094	23.432	29.547	25.491
ZnGaLDH_750	15.420	7.398	14.111	5.131	9.465	5.222
ZnGaLDH_925	30.063	26.385	19.867	25.869	33.860	16.284

Was noticed an improvement in the crystallinity of the ZnO in the sample ZnGaLDH as the calcination temperature was increased, showing stronger and sharper diffraction peaks in the sample calcined at 925°C.

The thermal decomposition of hydrotalcite-like compounds was studied. The thermal behaviour of the as-synthesized ZnGaLDH and ZnAlLDH precursor was examined by simultaneous TG/DTG/DSC analysis (Fig. 3 and Fig. 4).

As usual, the weight loss occurs essentially in two steps: the first one at low temperatures (25 – 165°C) corresponds to the removal of water physisorbed on the external surface of the crystallites as well as water intercalated in the interlayer galleries; the second weight loss at higher temperatures (175–395°C)

involves dehydroxylation of the layers as well as removal of the volatile species (CO_2) arising from the interlayer carbonate anions.

Two obvious endothermic peaks recorded at around 172 and 242°C (ZnGaLDH), respectively 175 and 236°C (ZnAlLDH) in the DSC curves correspond to the two weight loss steps. Moreover, the slight endothermic peak at around 613°C, without any weight loss accompanied, should be attributed to the rapid formation of $ZnGa_2O_4$ spinel (Zhang *et al*., 2014).

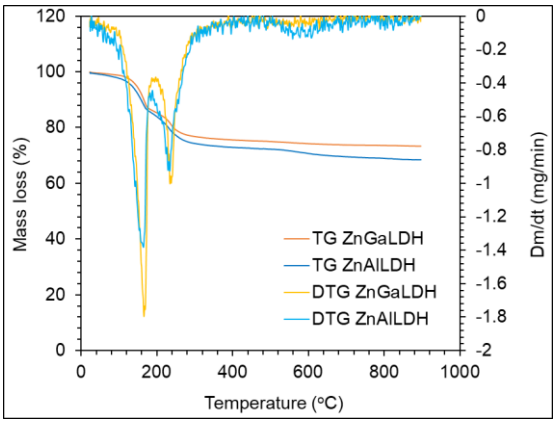

Fig. 3 − TG and DTG curves of ZnGaLDH and ZnAlLDH.

Table 1

Thermal analysis results

Sample	Characteristic temperatures, °C		% Mass loss
ZnGaLDH	165	238	26.82
ZnAlLDH	163	234	31.56

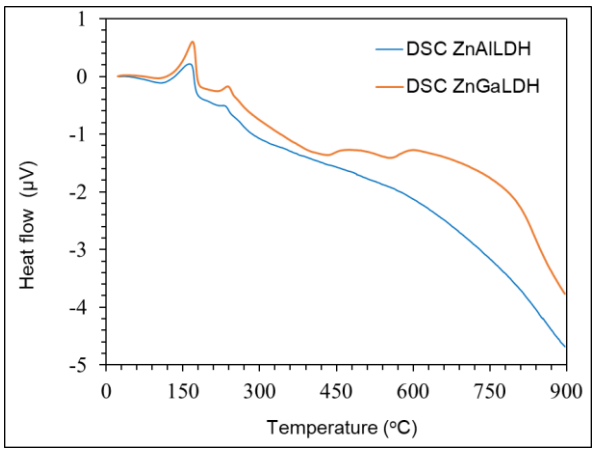

Fig. 4 − DSC curves of ZnGaLDH and ZnAlLDH.

4. Conclusions

ZnAlLDH and ZnGaLDH was fabricated by the co-precipitation method and the derived mixtures of mixed oxides were obtained by a thermal treatment at 750°C and 925°C, respectively. Detailed physical-chemical characterization use X-ray diffraction (XRD) and TG/DTG/DSC analysis was performed.

After the calcination at 750°C and 925°C, the layered structure of the 2-D Zn-rich LDH was destroyed. Calcination temperature plays a very important role in determining the degree of crystallinity and in determining the mixed oxides/spinels composition.

REFERENCES

Carja G., Gilea D., Cool P., Seftel E.M., *In Situ Synthesis of Bi_2O_3 Nanoparticles onZincMe (Me=Al or Cr) Layered Double Hydroxide Frameworks for Photocatalytic Oxygen Evolution from Water under Solar-Light Activation*, ChemCatChem., **10**, 1-10, (2018).

Ghribi F., Sehailia M., Aoudjit L., Touahra F., Zioui D., Boumechhour A., Halliche D., Bachari K., Benmaamar Z., *Solar-light promoted photodegradation of metronidazole over ZnO-$ZnAl_2O_4$ heterojunction derived from 2D-layered double hydroxide structure*, Journal of Photochemistry & Photobiology A: Chemistry, **397**, 112510, (2020).

Gilea D., Carja G., *XRD analysis of the structural properties of layered double hydroxides comprising Zn, Al partially substituted with Cu and Ce and derived mixed oxides*, Bull. Inst. Pol., **63** (67), 19-25, (2017).

Grosu E.F., Seftel E., Cuylcx M., Mertens M., Covaci A., Cool P., Carja G., *Efficient degradation and mineralization of diclofenac in water on ZnMe (Me: Al; Co; Ga) layered double hydroxides and derived mixed oxides as novel photocatalysts*, Comptes Rendus Chimie, **25**, 1-17, (2022).

Salih E.Y., Sabri M.F.M., Eisa M.H., Sulaiman K., Ramizy A., Hussein M.Z., Said S.M., *Mesoporous ZnO/$ZnAl_2O_4$ mixed metal oxide-based Zn/Al layered double hydroxide as an effective anode material for visible light photodetector*, Materials Science in Semiconductor Processing, **121**, 105370, (2021).

Salih E.Y., Ramizy A., Aldaghri O., Sabri M.F.M., Madkhali N., Alinad T., Ibnaouf K.H., Eisa M.H., *In-Depth Optical Analysis of Zn(Al)O Mixed Metal Oxide Film-Based Zn/Al-Layered Double Hydroxide for TCO Application*, Crystals, **12**, 79, (2022).

Zhang Y.X., Hao X.D., Wang T., Meng Y.X., Han X., *MnOx-modified ZnAl-LDOs as high-performance adsorbent for the removal of methyl orange*, Dalton Trans., **43**, 6667-6676, (2014).

UTILIZAREA STUDIILOR XRD ȘI TG/DTG/DSC PENTRU DESCRIEREA TRANSFORMĂRILOR STRUCTURALE INDUSE DE SUBSTITUȚIA Al^{3+} CU Ga^{3+} ÎN 2-D HIDROXIZI DUBLU LAMELARI ÎMBOGĂȚIȚI CU Zn

(Rezumat)

Modificările în caracteristicile structurale ale ZnMeLDH-urilor atunci când aluminiu a fost înlocuit cu galiu dar și transformarea lor în oxizi micști au fost evaluate prin difracție de raze X (XRD) și analiză termogravimetrică (TG/DTG/DSC). Rezultatele analizei XRD pentru ZnAlLDH și ZnGaLDH arată doar prezența LDH fără nicio impuritate, indicând ușoare diferențe între probele preparate cu diferiți cationi trivalenți, în raport cu volumul mai mare de Ga comparativ cu Al din cauza diferitelor raze cationice. După calcinare, structura LDH a fost distrusă și s-au obținut reflexiile XRD caracteristice oxizilor micști și spinelilor derivați. Rezultatele TG/DTG/DSC arată că pierderea de masă este similară pentru ZnAlLDH și ZnGaLDH. Se poate concluziona că atât compoziția LDH cât și temperatura de calcinare sunt parametri importanți care pot fi utilizați pentru a optimiza caracteristicile structurale ale ZnGaLDH și ale oxizilor micști omogeni de tip $ZnO/Ga_2O_3/ZnGa_2O_4$.